Lectures

on

Theoretical and Physical Chemistry

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PART III

RELATIONS BETWEEN PROPERTIES AND COMPOSITION

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PREFACE

THE present work on 'Relations between Properties and Composition' reproduces the lectures I gave in the Winter and Summer Sessions 1898–99 at the University of Berlin, under the title 'Selected Chapters in Physical Chemistry.' It follows, as third and last section, the first and second on 'Chemical Dynamics' and 'Chemical Statics' respectively, but is arranged as far as possible independently and covers the relations of physical and chemical properties to constitution, only with certain limitations. Some of these relations are exact, and available for determining constitution itself: these belong properly to Part II. Others have at present a character so decidedly empirical that they belong rather to systematic chemistry.

Hence in the region of physical properties I have dealt only with what can directly or indirectly be brought into connexion with the characteristic equation. Although this does not afford a strictly trustworthy physical basis, like Thermodynamics in Part I and the limit-laws for the dilute state in Part II, still the point of view brings out many approximate regularities.

In the relations between chemical properties and constitution I have mostly restricted myself to those properties that can easily be reduced to numerical expression.

The fact that the first part of these lectures has already been translated into French and English may serve as a recommendation to this last part.

It is, finally, a pleasant duty to express my warmest thanks to Drs. W. Meyerhoffer and J. J. van Laar for the revision and emendation of this work.

J. H. VAN 'T HOFF.

CONTENTS OF PART III

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THE DIVISION OF THE WORK AND
THE TREATMENT CHOSEN

In the inevitably arbitrary division of any subject it is well to choose so that it may easily be seen where each part belongs. For this reason the treatment adopted by Lothar Meyer in the later editions of his *Modern Theories of Chemistry* seemed to me appropriate for my lectures: in it the whole is divided into Statics and Dynamics. Statics then deals with single substances, i. e. with views on the structure of matter, the conception of atoms and molecules, and on constitution so far as the determining of molecular configuration. Dynamics is devoted to the mutual actions of several substances, i. e. to chemical changes, affinity, velocity of reaction, and chemical equilibrium.

To these I have added a third section, in which the chief object is the comparison of one substance with another, and consequently the relations between properties—both chemical and physical—and composition.

In preparing for the press I have preserved this arrangement, only making a change in the order in accordance with the development of chemical science in the last ten years. Until then Dynamics, that is the study of reactions and of equilibrium, took a secondary place. But lately, and especially since the study of chemical equilibrium has been related to thermo-dynamics, and so has steadily gained a broader and safer foundation, it has come into the foreground of the chemical system, and seems more and more to belong there.

The following arrangement is therefore chosen as an experiment :—

    First Part : Chemical Dynamics.

    Second Part : Chemical Statics.

    Third Part : Relations between Properties and Composition.

The logical advantage gained in this way is essentially that in the First Part it is possible to proceed without any hypothesis on the nature of matter. only the molecular conception being made use of. Not till the Second Part does the atomic hypothesis come to the front, and with it problems of configuration. Finally comes the still very obscure problem of the relation of one body to another.

There are two points, however, that should be referred to. From the logical side it may be objected that Statics is concerned with the simpler problem, since it deals with single substances at rest, whereas Dynamics deals with a complex of substances in action. This objection, however, has less force when one remembers that the single substance corresponds to the state of equilibrium following a completed reaction and indeed the simplest form of equilibrium—and accordingly Part II is devoted to the more detailed study of this final state.

From the paedagogic point of view, placing Dynamics first can be dubious only to those chemists who are not well prepared in Physics, and consequently have not mastery over the chief lines of their own subject.

The treatment chosen corresponds with that I have followed in teaching. It consists essentially in developing each generalization from a specially chosen concrete experimental case. On this follow an exhibition—as far as possible graphic—of the leading results, the conclusions drawn, and, lastly, theoretical remarks on the generality and applicability of the conclusions.

PART III

RELATIONS BETWEEN PROPERTIES AND COMPOSITION

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Contents and arrangement. Since in Part II of this work we have traced how the constitutional and configurational formula has been developed into an expression of the material structure, we have now, in the present part, to discuss the relations which hold between that structure and the properties of bodies. Fundamentally Part II is concerned with the same problem, for the configurational formula is a more or less successful symbolic representation of those properties from which it is derived. Here, however, a distinction may be made. There are properties, such as the quantitative composition of a compound, the density of a gas, and so on, whose connexion with the chemical formula is so far certain, that they may be regarded as directly deducible from the formula in question, as a necessary consequence of the assumed atomistic and molecular concepts. On the other hand there are relations holding between composition and properties that so far have only an empirical value, or with more or less theoretical support carry in them the germs of relations that might serve for the determination of chemical formula,

molecular weight, &c. It is with this class of relations t
we are now concerned.

The arrangement will be, according as we are dea
with physical or chemical properties :

I. Relations between physical properties and com
sition.

II. Relations between chemical properties and com
sition.

I. RELATIONS BETWEEN PHYSICAL PROPERTIES AND COMPOSITION

In dealing with physical properties with regard to their relations to composition, a preliminary study is needed in order to refer the property in question, so far as the body under consideration is concerned, to one or more constant quantities. If we take as example the state of aggregation, it is obvious that the boiling point is not such a constant quantity. On comparing benzene with ethyl alcohol:

	Boiling point under 222 mm.	*under 2256 mm.*
Benzene	45°	120°
Ethyl alcohol	50°	106°

we find that the difference of boiling points even changes sign through change of pressure, as at low pressure alcohol, at high pressure benzene, has the higher boiling point.

Before any relation can be found between boiling point and composition, then, that between boiling point and pressure must be explained, so that the preliminary study referred to appears in general as the relating of the property considered to its circumstances.

Such a preliminary study has hitherto only been partially carried out in the form of the so-called characteristic equation, and that only for amorphous, i. e. for liquid and gaseous states. In crystalline bodies the orientation of the substance involves complications that have retarded the solution of the problem, which even for amorphous bodies has only been given very imperfectly.

We will therefore confine ourselves to gases and liquids, and further, to those properties which are more or less directly connected with the characteristic equations. Since we adopt these equations as basis it should be remarked that we are here dealing with physical relations of a different order to those previously used. In dynamics it was, on the physical side, mainly the two fundamental laws of thermo-dynamics ; in statics the limit-laws of Boyle, Gay-Lussac, and Avogadro were invoked, and they may claim strict applicability at least to the state of infinite dilution as gas or solution. The characteristic equations, on the other hand, are merely more or less rationally founded interpolation formulae, which are only strictly in accord with the facts for the state of infinite dilution, and then resolve themselves into the former laws. As a consequence of this the treatment following must be essentially different. Whilst the fundamental laws of thermo-dynamics, and the limit-laws for infinite dilution serve to control experimental results, here, on the contrary, an accepted relation must often be modified to suit the facts, yet mostly in such a way that something of it remains which could not so easily be made out from the facts alone. From this again follows the essential point that the relations obtained on account of their partly empirical character only allow of conclusions as to molecular weight and constitution, inferior in certainty to those of Part II.

§ 1. VOLUME RELATIONS.

Since in dealing with volume relations we are concerned with the relations to chemical constitution, we will adopt a corresponding arrangement, and first consider the relations which depend on the number of molecules, called by Ostwald colligative, and which may serve as a guide to determining molecular weights. Afterwards will come the additive and constitutive relations, which depend on the composition of the molecule.

A. Colligative Relations.

1. *Characteristic Equation.*

General. The preliminary problem as to the connexion between properties and the circumstances of the substance has first been followed out with success as regards volume, and as is well known has yielded a satisfactory result for dilute gases.

The influences which change the volume (V), namely the pressure (P) and temperature (T in absolute centigrade measure), are determined by the laws of Boyle and Gay-Lussac, which are completely expressed by the equation

$$PV = RT;$$

this equation has moreover a theoretical basis in the kinetic theory of gases, according to which the pressure, being due to molecular collisions, is directly proportional to the number of collisions, and therefore inversely to the volume, whilst to explain the increase of pressure due to temperature, it is assumed that the kinetic energy of molecular movement is proportional to the absolute temperature.

The relation between volume and composition takes, in accordance with this result, a very simple form, being contained in Avogadro's law, according to which molecular quantities under the same pressure and temperature occupy the same volume, thus R is the same for all gases, provided the molecular quantity be considered, as is shown by the equation already given (Part II, p. 19)

$$APV = 2T,$$

where $A = \dfrac{1}{423}$, P is the pressure in kilograms per square metre, V the volume of a kilogram molecule in cubic metres.

This relation, which may also be based on the kinetic theory, is, it is well known, so trustworthy that it serves as a safe means of determining the molecular magnitude, and was treated as such in Part II.

It is different as soon as the gas departs from the ideal state of dilution. Take e. g. the values of the product PV for ethylene at 20° and high pressure :

| $P =$ 31·58 atm. | 84·16 atm. | 398·71 atm. |
| $PV =$ 0·914 ,, | 0·399 ,, | 1·248 ,, |

The above fundamental equation for perfect gases has to be transformed into the so-called characteristic equations in order to account for such deviations. None of them is strictly rationally based, and in satisfactory agreement with the facts, else it would be possible to obtain a reliable insight into the molecular weights of liquids also. Still colligative relations may be shown, on the strength of these characteristic equations, which give a point of departure for molecular weight determinations, and must therefore be considered here.

Budde[1] pointed out the necessity for a correction on account of the volumes of the gas molecules, and put instead of the total volume, V, a quantity smaller by the constant b,

$$P\,(V-b) = RT.$$

Van der Waals[2] pointed out the equally necessary correction for the molecular attraction, by which the pressure directed outwards, P, is reduced. Assuming this attraction as a first approximation to be inversely proportional to the square of the volume, he obtained

$$\left(P + \frac{a}{V^2}\right)(V-b) = RT.$$

Clausius[3] showed the assumption that the attraction depends only on the volume to be inadmissible and preferred :

$$\left\{P + \frac{a}{T(V+\beta)^2}\right\}(V-b) = RT;$$

whilst it appeared later that a more complicated formula[4] is

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[1] *Journ. f. Prakt. Chem.* 9. 30.

[2] *Continuity of the Gaseous and Liquid States.*

[3] *Wied. Ann.* 9. 337.   [4] l. c. 14. 279.

needed to agree with the facts, and such were suggested by Sarrau[1], Batelli[2], and Jäger[3].

Van der Waals[4] endeavours to take this circumstance into account by the expression

$$\left(P + \frac{ae^{1-\frac{T}{T_k}}}{V^2}\right)(V-b) = RT;$$

but then b appears only to be constant to a first approximation, and should be replaced by[5]

$$b\left(1 + a\,\frac{b}{V} - \beta\,\frac{b^2}{V^2} + \gamma\,\frac{b^3}{V^3}\cdots\right),$$

in which $\qquad a = \dfrac{17}{32}, \quad \beta = 0\cdot0958$[6];

whilst lately, Amagat[7], Rose-Innes[8], and Lewis[9] have made other suggestions.

None of these equations can be regarded as the expression of a natural law: in deducing them, simplifying assumptions are always made, and in none of them has complete agreement with the facts been proved. Under these circumstances it is best to choose the one which forms the best compromise between accuracy and simplicity.

The equation

$$\left(P + \frac{a}{V^2}\right)(V-b) = RT,$$

seems the most suitable. This expresses the qualitative behaviour, indicating the gaseous state, the critical phenomena, and the formation of liquid; only the solid state of aggregation is not accounted for, which is due to the deduction assuming spherical molecules, and consequently

[1] *Zeitschr. f. Phys. Chem.* 12. 280. [2] *Memorie di Torino*, 1893, p. 27.
[3] *Wien. Akad. Ber.* 1892, p. 1675 ; see also p. 35.
[4] Van Laar, *Die Thermo-dynamik in der Chemie*, 1893, p. 50 ; *Zeitschr. f. Phys. Chem.* 11. 433.
[5] Van der Waals, *Verslagen Kon. Akad.* Amsterdam, 1898.
[6] Van Laar, *Archives Teyler*, 1899.
[7] *Comptes Rendus*, 1894, p. 566. [8] *Phil. Mag.* 1899. p. 367.
[9] Amer. Acad. of Sc. 1899 ; see also O. E. Meyer, *Kinetic Theory of Gases*, 1899 ; Thiessen, 'Zustandsgleichungen,' *Wied. Ann.* 1898.

paying no attention to molecular orientation. The equation does not correspond quantitatively to the facts, but often gives valuable indications, which may be extended into empirical rules by experiment.

Qualitative test of the characteristic equation. Beginning with the qualitative test, it must be noted first that for large values of V the original simple expression

$$PV = RT$$

is recovered, since b is small compared with V and $\dfrac{a}{V^2}$ compared with P. It may be added that this condition must be satisfied by any characteristic equation; so that the general formula

$$PV - RT = F$$

becomes necessary, F being a function which is zero for indefinitely great values of V.

Representing the values of P and V in the above equation graphically for fixed temperatures, i.e. by drawing iso-

thermals, P upwards, V to the right, in Fig. 1, for each temperature there will be on the right a part of a rect-angular hyperbola.

For further guidance let us determine [1] the value of

$$\frac{dP}{dV}$$

at constant temperature, i.e.

$$\frac{dP}{dV} = \frac{2a}{V^3} - \frac{RT}{(V - b)^2}.$$

Fig. 1.

For large values of T this gives always a negative value for $\dfrac{dP}{dV}$ and consequently a curve like 1.

Further, for small values of V, since $V - b$ approaches zero
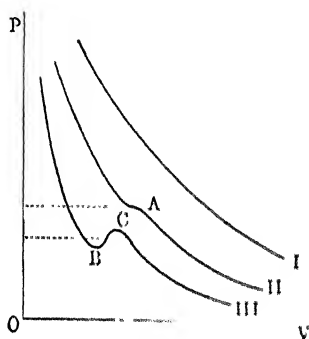
[1] Boltzmann, *Vorlesungen über Gastheorie*, 1898.

$\dfrac{dP}{dV}$ is again negative, so that the left portions of II and III run like I.

But as soon as $\dfrac{2a}{V^3} - \dfrac{RT}{V-b} = 0$

a horizontal tangent appears somewhere, as on the isothermal II at A since $\dfrac{dP}{dV}$ is zero; whilst if the temperature is still lower positive values of $\dfrac{dP}{dV}$ arise, and the curve III has consequently a bend upwards towards the right as at BC.

Physically this isothermal III corresponds to the possibility of three volumes (F, o, and E, Fig. 2) for one pressure. Of these three that at o is unstable since here for increasing pressure there is an increase in volume, and consequently a further increase in pressure; hence only two possibilities remain, corresponding to the liquid volume F and the vapour volume E, and the empirical curve becomes D F O E instead of D F B O C E,
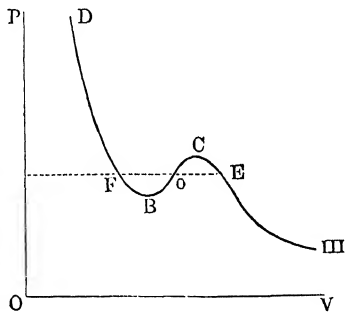
Fig. 2.

since at E condensation occurs, and the volume is reduced in presence of liquid and vapour together, by increase in the quantity of the former at constant pressure till finally at F only liquid remains, and the pressure begins to rise again.

Curve I therefore shows the continuous compression without partial condensation; curve II the limiting temperature for which at A a small reduction of temperature causes separation into liquid and vapour, as in curve III; II therefore shows the critical temperature.

It may be added that the position of EF is fixed by

means of a reversible cyclic process at constant temperature, performed along C O B F O E C. Since without fall of temperature there can be no work produced or consumed, the area of C E O C must be equal to that of B F O B.

With regard to the characteristic equation in general, we may say that the requisite qualitative agreement with the facts depends on the equation being of the third degree in V, so that equations of the first or second degree in V, like that of Budde (p. 16), are inadmissible as characteristic equations.

Quantitative test of the characteristic equation. The quantitative test may be carried out in two directions, first as to how far the constants a and b account for the deviations from Boyle's law, and then how far the critical data can be calculated from a and b. The following table, referring to ethylene at $20°$, allows of a conclusion on the first point; it is calculated[1] from the equation

$$\left(P + \frac{0.00786}{V^2}\right)(V - 0.0024) = 0.0037 \, (272.5 + t).$$

P	1000 PV		P	1000 PV	
	obs.	calc.		obs.	calc.
31·58	914	895	133·26	820	820
45·80	781	782	176·01	643	642
59·38	522	624	233·58	807	805
72·86	416	387	282·21	941	940
84·16	399	392	329·14	1067	1067
94·53	413	413	398·71	1248	1240
110·47	456	456			

Here the atmospheric pressure is taken as unit for P, and for V the volume which the given quantity of ethylene takes at $0°$ and one atmosphere.

The conditions for the critical point, i.e. temperature pressure and volume at A in Fig. 1, the so-called critical data $T_k \, P_k \, V_k$ may be calculated by putting the equation in the more general form:

$$V^3 - \left(b + \frac{RT}{P}\right)V^2 + \frac{a}{P} \, V - \frac{ab}{P} = 0.$$

[1] Baynes, *Nature*, 22. 186.

For temperatures below A three roots are possible:

$$V = V_1, \qquad V = V_2, \qquad V = V_3,$$

and the equation becomes

$$(V - V_1)(V - V_2)(V - V_3) = 0.$$

At A the three roots become equal:

$$V_1 = V_2 = V_3 = V_k,$$

and the equation is

$$(V - V_k)^3 = V^3 - 3V_k V^2 + 3V_k^2 V - V_k^3 = 0;$$

hence

$$b + \frac{RT_k}{P_k} = 3V_k \ (1), \quad \frac{a}{P_k} = 3V_k^2 \ (2), \quad \frac{ab}{P_k} = V_k^3 \ (3);$$

so that

$$V_k = 3b \ \text{ from (2) and (3)};$$

$$P_k = \frac{a}{27b^2} \ \text{ from (2)};$$

$$T_k = \frac{8a}{27bR} \ \text{ from (1)}.$$

We accordingly find for ethylene

$$T_k = \frac{8 \times 0 \cdot 00786}{27 \times 0 \cdot 0024 \times 0 \cdot 0037} = 262° \text{ absolute, i.e. } -11° \text{ C.}$$

(observed 282° abs., i.e. 9° C.[1]).

$$P_k = \frac{0 \cdot 00786}{27 \times 0 \cdot 0024^2} = 50 \cdot 5 \ (\text{observed } 51);$$

$$V_k = 0 \cdot 0072 \ (\text{observed } 0 \cdot 006).$$

Whilst, therefore, the qualitative behaviour of gases, including condensation up to the critical temperature, and the formation of liquid is in agreement with the equation, the quantitative data as to critical temperature may also to a certain extent be brought into accord with the values of *a* and *b*, determined from the deviations from the laws of Boyle and Gay-Lussac.

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[1] Landolt, *Börnstein*, p. 84.

2. *Introduction of Avogadro's Law into the Characteristic Equation.   Constant Ratio between the Theoretical and Critical volume* [1].

Avogadro's law may most conveniently be introduced into the characteristic equation by considering the molecular quantity of the substances in question.

As in the limiting equation

$$PV - RT = 0,$$

so in the characteristic equation

$$PV - RT = F.$$

R is the same for all bodies, and, in fact, the same as is derived from the limiting equation.

In the special characteristic equation adopted on p. 21, since

$$b + \frac{RT_k}{P_k} = 3V_k, \qquad \frac{a}{P_k} = 3V_k{}^2, \qquad \frac{ab}{P_k} = V_k{}^3 ;$$

a and b may be eliminated, and we get

$$\frac{RT_k}{P_k} = 3V_k - b = 3V_k - \tfrac{1}{3}V_k = \tfrac{8}{3}V_k ,$$

or

$$\frac{P_k V_k}{T_k} = \tfrac{3}{8}R,$$

so that $\dfrac{P_k V_k}{T_k}$ would have a constant value calculable from the laws of perfect gases.   The following table gives the results of the calculation:

Substance	$T_k - 273$	P_k in atm.	V_k	$\dfrac{P_k V_k}{T_k}$
Ether	194	35·6	301	22·4
Ethyl acetate	250	39·7	294	22·3
Ethyl butyrate	293	30·2	421	22·5
Ethylene chloride . . .	288	53	220	20·7
Ethyl formate	233	49·2	235	22·8
Ethylidene chloride . .	250	50	236	22·6
Ethyl isobutyrate . . .	280	30·1	422	22·9
Ethyl propionate . . .	272	34·6	357	22·7
Alcohol	243	63	168	20·4

[1] *Chem. Centr. Bl.* 1898, II. 1073.

Substance	$T_k - 273$	P_k in atm.	V_k	$\dfrac{P_k V_k}{T_k}$
Amyl formate	303	34·1	412	24·4
Benzene	289	47·9	256	21·8
Chloro-benzene. . . .	361	44·7	307	27·6
Hydrochloric acid . . .	52	86	60	22·6
Fluor-benzene	289	44·6	271	21·6
Isobutyl acetate . . .	288	31·4	413	23·1
Carbon dioxide	31	77	98	24·8
Oxygen	−118	50	53	17·1
Carbon disulphide . .	273	72·9	215	28·7
Nitrous oxide	36	73·6	108	25·4
Water	364	194·6	87	26·4
Stannic chloride . . .	319	37	349	21·8

The values in question are therefore moderately constant, averaging 22, but differ considerably from the expected $\frac{3}{4} R$, as e.g. oxygen at 0° and 1 atm. gives

$$R = \frac{PV}{T} = \frac{32}{273 \times 0·00143} = 82.$$

Instead of $\frac{3}{8} = \frac{1}{2·7}$ we find $\frac{22}{82} = \frac{1}{3·7}$, i.e. the theoretical number divided by about $\sqrt{2}$.

This rule—in the first place an empirical one—due to Young and Thomas, may be expressed in another way. The relation

$$\frac{P_k V_k}{T_k} = \frac{R}{3·7}$$

states that the critical volume is $\frac{1}{3·7}$ times that calculated from the usual equation to a gas, or that the critical density P_k is 3·7 times the theoretical density.

At the same time a third condition for the characteristic equation is thus arrived at, and at least a point of departure for judging of the molecular weight in the critical condition. Let us apply the result to gases.

Thus to determine the molecular weight of carbon tetrachloride and acetic acid in the critical state we have :

	D_k	P_k	T_k
CCl_4	0·556	44·9	273 + 283
$C_2H_4O_2$	0·407	57·1	273 + 322

and since

$$V_k = \frac{M}{D_k},$$

the fundamental equation becomes

$$\frac{MP_k}{D_k T_k} = 22.$$

For carbon tetrachloride

$$M = \frac{22 \times 0.556 \times 556}{44.9} = 151; \quad (CCl_4 = 154);$$

for acetic acid

$$M = \frac{22 \times 0.407 \times 595}{57.1} = 93; \quad (C_2H_4O_2 = 60).$$

Whilst, therefore, carbon tetrachloride behaves normally, the result indicates that acetic acid in the critical state contains double molecules, as also follows with certainty from the vapour density, and from investigation of solutions in hydroxyl free solvents such as benzene.

3. *Corresponding States.*

If in the characteristic equation

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT,$$

pressure, volume, and temperature are expressed in terms of the critical values as units, i. e.

$$P = aP_k, \qquad V = \beta V_k, \qquad T = \gamma T_k,$$

and a, b and R eliminated, then since (p. 21)

$$\frac{a}{P_k} = 3V_k^2 \text{ or } a = 3V_k^2 P_k;$$

$$V_k = 3b \text{ or } b = \tfrac{1}{3}V_k;$$

$$T_k = \frac{8a}{27bR} \text{ or } R = \frac{8a}{27bT_k} = \frac{8V_k P_k}{3T_k};$$

we obtain

$$\left(a P_k + \frac{3 P_k}{\beta^2} \right) \left(\beta V_k - \frac{V_k}{3} \right) = \frac{8 \gamma V_k P_k}{3} ,$$

or

$$\left(a + \frac{3}{\beta^2} \right) (3\beta - 1) = 8 \gamma .$$

In testing this so-called reduced characteristic equation by the facts, it will appear that it does not represent the behaviour of a particular substance[1], but that it is very suited to bring out the corresponding character of different bodies.

The first point will be plain on calculating

$$\frac{\left(a + \frac{3}{\beta^2} \right) (3\beta - 1)}{\gamma} = F$$

from the data for the best investigated substance—fluorbenzene.

$\gamma = \frac{T}{T_k}$	$a = \frac{P}{P_k}$	$\beta_1 = \frac{V}{V_k}$ (liquid)	F_1	$\beta_2 = \frac{V}{V_k}$ (vapour)	F_2
1	1	1	8	1	8
0·929	0·589	0·536	6·6	3·73	9·7
0·823	0·236	0·448	6·3	10·6	9·8
0·733	0·088	0·407	5·5	28·4	10·7
0·700	0·055	0·396	5·2	44·0	10·6
0·656	0·029	0·381	3·6	81·4	10·7
0·605	0·012	0·366	3·6	167	9·9
0·487	0·006	0·338	0·8	500	18·5

The values of F which should be constantly 8 vary greatly, being too low for liquid, too high for vapour.

Still on comparing substance with substance striking relations appear, dependent on the fact that a reduced characteristic equation, such as that under consideration, represents the behaviour of all substances by a single isothermal for each value of γ. Referred to the volume that means that at equal fractions of the critical temperatures, the liquid volumes are equal fractions, and the vapour

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[1] Riecke, *Gött. Nachr.* 1894.

volumes equal multiples of the critical volume, whilst the
ratio of liquid and vapour volumes, or densities, is a con-
stant quantity for each value of γ.

To confirm this rule we will apply it e.g. to hexane, and
calculate the density as liquid and as saturated vapour at
a given temperature, say $82°$. Since the critical tempera-
ture is $235°$ the fraction in question,

$$\gamma = \frac{273 + 82}{273 + 235} = 0.7.$$

From the preceding table for fluor-benzene we find that
at this fraction of the critical temperature the liquid volume
(β_1) is 0.396 of the critical volume, while the volume of the
saturated vapour is 44 times the latter. Since the critical
density of hexane has been found to be 0.2343, those of the
liquid and vapour at $82°$ are

$$\frac{0.2343}{0.396} = 0.592 \text{ and } \frac{0.2343}{44} = 0.0053.$$

whilst 0.599 and 0.005 were actually found.

Let us see next how far the behaviour in question gives
a point of departure for judging of molecular weights.
Striking deviations are observed in the alcohols. If
we take ethyl alcohol, for example, and compare it with
benzene, choosing the ratio of volumes at the critical points
as unit:

$\gamma = \dfrac{T}{T_k}$	$\dfrac{\beta_1'}{\beta_1''}$ liquid	$\dfrac{\beta_1'}{\beta_1''}$ saturated vapour
1	1	1
0.928	0.99	1.24
0.822	0.99	1.74
0.733	0.99	2.30
0.656		3.51
0.639	1.01	

The second column gives the volume of the liquid alcohol
referred to that at the critical point, divided by the corre-
sponding quotient for benzene: the third column gives the
same for saturated vapour. The rules of corresponding states
require that all these quotients should be unity. This is

very nearly the case for the liquid, but not at all for the vapour. On the other hand there is evidence that the molecular magnitude, which is nearly normal at the critical point, as appears from p. 23, is increased in the liquid on fall of temperature by formation of double molecules ; the osmotic methods, in fact, give for liquid alcohol dissolved in hydroxyl-free solvents, abnormally high values (Part II, p. 60), which indicates the same conclusion as to liquid alcohol itself at ordinary temperature. But alcohol vapour at ordinary temperature possesses the normal density.

The striking fact that the formation of double molecules which takes places in solution and not in vapour should give rise to abnormal relations in the vapour only may be explained by the following considerations : imagine a liquid, say ethyl alcohol, in equilibrium with its saturated vapour, and assume that each has the normal molecular weight corresponding to C_2H_6O, and that the density of liquid and vapour obey the rule of corresponding states. Now let some of the simple molecules in the liquid be converted into double ones; the kinetic equilibrium due to the equal evaporation and condensation of molecules C_2H_6O is now upset, since fewer evaporate. Accordingly fewer must condense, so that a reduction in the amount of the vapour must take place, causing a decrease in its density and pressure, but an increase in the volume of a given weight, as the above numbers indicate.

If, further, we accept the law of correspondence as a further condition for the characteristic equation, it is to be remarked that any equation that has as many characteristic variables (P, V, T) as constants (a, b, R), i.e. of the form

$$f\ (P,\ V,\ T,\ a,\ b,\ R) = 0,$$

leads to the same conclusion if it includes the critical state [1].

[1] Meslin, *Compt. Rend.* 116. 135.

4. The Rectilinear Diameter [1].

Since it appears from the preceding that the volume relations of various substances are inter-related we will return to one of them, fluor-benzene, as type; we then find that despite the failure of the reduced characteristic equation, a very simple relation of volumes holds, which, however, must so far be treated as purely empirical. It is the so-called rule of the rectilinear diameter which states that the sum of the densities of liquid and saturated vapour is a linear function of the temperature, as may be seen from the following data in which the critical values are chosen as units of temperature and density:

$\gamma = \dfrac{T}{T_k}$	$\dfrac{1}{\beta_1} = \dfrac{V_k}{V}$ (liquid)	$\dfrac{1}{\beta_2} = \dfrac{V_k}{V}$ (sat. cap.)	$\dfrac{\Delta\left(\dfrac{1}{\beta_1} + \dfrac{1}{\beta_2}\right)}{\Delta\gamma}$
1	1	1	
0·929	1·863	0·206	1·82
0·823	2·231	0·004	1·85
0·733	2·457	0·045	1·80
0·656	2·628	0·012	1·92
0·605	2·730	0·006	1·88
0·487	2·956	0·002	1·88

Fig. 3 reproduces this relation, expressed directly in density and temperature: AB expresses the density of the liquid D_l, BC that of the saturated vapour D_v, B the critical density D_k; the diameter BD expresses the values of $\frac{1}{2}(D_l + D_v)$, its straight course is therefore the expression of the law in question, which may also be represented by the equation

$$D_l + D_v = a - bT.$$

Fig. 3.

When double molecules are found in the liquid, as in the case of alcohol according to the
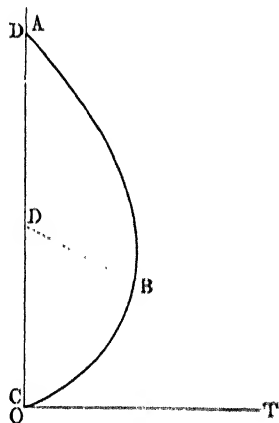
data on p. 26, a corresponding departure from the rule is to be expected, as is shown by the following table:

$\gamma = \dfrac{T}{T_k}$	$\dfrac{1}{\beta_1} = \dfrac{V_k}{V}$ (liquid)	$\dfrac{1}{\beta_2} = \dfrac{V_k}{V}$ (sat. vap.)	$\dfrac{\Delta\left(\dfrac{1}{\beta_1} + \dfrac{1}{\beta_2}\right)}{\Delta\gamma}$
1	1	1	—
0·928	1·863	0·216	1·1
0·822	2·231	0·054	2
0·733	2·457	0·015	2·1
0·656	2·628	0·004	2·1
0·605	2·730	—	1·9

The deviation thus appears at the beginning, near the critical temperature; at low temperatures the density of the vapour, which also is abnormal, is of little consequence, so that the normal value 1·9 reappears.

5. *Volume at the Absolute Zero* [1].

Whilst in dealing with volume relations we keep as closely as possible to experimentally accessible quantities, we must now consider what is the least possible volume a given mass of substance can take up, i. e. the volume at the absolute zero. This quantity is, of course, not completely accessible to experiment, but with the means of reaching low temperatures now available it ought soon to be possible to arrive at the volume at the absolute zero by means of a reasonable extrapolation.

Making use, therefore, of the law of the rectilinear diameter, we will calculate the ratio between the density at the absolute zero (D_0) and the critical density (D_k) by means of the value at the freezing point (D), since for the substance in question the density of the vapour at that temperature may be neglected. Then if t_k is the critical temperature in centigrade degrees we have:

$$D_0 = D + \frac{(D - 2\,D_k)\,273}{t_k}.$$

In that way the following table is obtained:

[1] Guldberg, *Chem. Centr. Bl.* 1898; 2. 1042.

Substance	D_k	V_k	D	$D_0 : D_k$
C_6H_6	0·304	289	0·900	3·87
C_6H_5F	0·354	289	1·047	3·87
C_6H_5Cl	0·367	361	1·128	4·06
CH_3OH	0·277	240	0·822	4·06
C_2H_5OH	0·279	243	0·807	3·89
C_3H_7OH	0·278	264	0·820	3·95
$(C_2H_5)_2O$	0·263	194	0·736	3·92
CH_3CO_2H	0 352	322	1·080	3·97
CCl_4 . . ·	0·556	283	1·632	3·86
$SnCl_4$	0·742	319	2·279	4·00
C_6H_{12}	0·273	280	0·797	3·81
C_6H_{14}	0·234	235	0·677	3·92
Methyl formate . . .	0·349	214	1·000	3·97
Ethyl formate	0·323	235	0·948	4·03
Propyl formate . . .	0·310	265	0·929	4·03
Methyl acetate . . .	0·326	234	0·959	4·04
Ethyl acetate	0·308	250	0·924	4·09
Propyl acetate	0·296	276	0·910	4·14
Methyl propionate . .	0·312	257	0·939	4·07
Ethyl propionate . . .	0·297	273	0·912	4·14
Methyl butyrate . . .	0·300	281	0·920	4·10
Methyl isobutyrate . .	0·302	268	0·911	4·06

The density at the absolute zero is, therefore, in accordance with the position of this temperature as the corresponding temperature $\dfrac{T_k}{\infty}$, a fairly constant multiple, about four times the critical density. This agrees with the results obtained from measurements on pentane at the lowest temperatures [1]; this at $-189°$ has a density of 0·869 approximately ($t_k = 188$, $D_k = 0·235$, $D_0 : D_k = 4·08$), whilst from the reduced characteristic equation for fluor-benzene (p. 28) we get

$$2·956 + \frac{2·956 - 2}{1 - 0·487} \times 0·487 = 3·89.$$

We may add that the characteristic equation employed partly answers to this result, since in

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT,$$

for $T = 0$, $V_0 - b = 0$,   therefore $V_0 = b$.

[1] *Zeitschr. f. Phys. Chem.* 23. 371.

But according to what precedes (p. 21),

$$b = \tfrac{1}{3} V_k,$$

therefore $\qquad\qquad V_0 = \tfrac{1}{3} V_k;$

i. e. equally a constant ratio between the volume at the critical point and the critical volume, only $\tfrac{1}{3}$ instead of the experimental $\tfrac{1}{4}$.

6. *Volume of the Liquid at Low Temperature* [1].

By applying the three empirical rules—(1) as to critical density, (2) density at the absolute zero, (3) of the rectilinear diameter, a good insight may be obtained into the volume relations of liquids at temperatures such that the density of the vapour may be neglected by comparison with that of the liquid, i.e. at temperatures not very close to the critical point.

The law of rectilinear diameter connects the liquid and vapour densities (D_l and D_v) by the equation

$$D_l + D_v = a - bT,$$

in which, according to (2), for

$$T = 0, \qquad D_v = 0, \qquad D_l = 4 D_k,$$

so that $\qquad\qquad a = 4 D_k,$

and for $\qquad\qquad T = T_k, \qquad D_l = D_v = D_k.$

Therefore

$$2 D_k = 4 D_k - b T_k, \qquad b = \frac{2 D_k}{T_k},$$

so that

$$D_l + D_v = 4 D_k - \frac{2 D_k T}{T_k} = \frac{2 D_k (2 T_k - T)}{T_k},$$

and if D_v is negligible

$$V = \frac{1}{D} = \frac{T_k}{2 D_k (2 T_k - T)} = \frac{V_k T_k}{2 (2 T_k - T)},$$

in which, according to (1),

$$V_k = \frac{R T_k}{3 \cdot 7 P_k}.$$

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[1] D. Berthelot, *Compt. Rend.* **128. 606.**

Referred to the molecular quantity in grams with P in atmospheres, according to p. 23,

$$R = 82,$$

so that

$$V = \frac{82\,T_k^2}{7\cdot4\,P_k\,(2\,T_k - T)} = \frac{11\cdot1\,T_k^2}{P_k\,(2\,T_k - T)}.$$

This relation may be tested in certain cases as follows :

	T	D	T_k	P_k	$V = \dfrac{M}{D}$	V (calc.)
N_2	78·6	0·885	127	33	31·6	30·9
NH_3	274	0·635	403	115	26·9	29·5
$SnCl_4$	273	2·279	592	39·6	115	108
Ethyl isobutyrate .	273	0·89	553·4	30·1	130	135
C_6H_5I	288	1·831	721	44·7	111	112

One is inclined to go a step further, and use the above relation to determine molecular weights by means of the density of liquids ; thus from

$$\frac{M}{D} = V = \frac{11\cdot1\,T_k^2}{P_k\,(2\,T_k - T)},$$

M may be determined by means of $D\ T_k\ P_k$ and T. This would serve in the case of the above-mentioned substances, and from a collection of forty-two[1] it appears that the maximum error is 9 %, which is usually not too great for a molecular weight measurement.

The important question as to double molecules in liquids is, however, not satisfactorily answered in this way. If the doubling has already set in at the critical point, which appears to be the case with acetic acid, the values of P_k and T_k are influenced by it, and the calculated molecular volume or weight becomes abnormal :

	T	D	T_k	P_k	$V = \dfrac{M}{D}$	V (calc.)
$C_2H_4O_2$	273	1·08	594·6	57·1	57	75

But if the doubling occurs first below the critical point, as is apparently the case for ethyl alcohol (p. 26), it all depends on whether this fact affects the liquid density,

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[1] D. Berthelot, *Compt. Rend.* 128. 606.

which, according to p. 26, is not largely the case for ethyl alcohol, since liquid alcohol approximately follows the law of correspondence. The data are as follows :

	D	T	T_k	P_k	$V = \dfrac{M}{D}$	V (calc.)
Water . . .	0·999	289	638	195	18	23·5
Methyl alcohol	0·796	293	513	68·5	40·3	58·2
Ethyl alcohol .	0·789	293	517	64·3	58·4	62·3
Propyl alcohol .	0·788	289	531	50·2	76·2	80·7

The chief criterion of molecular doubling, so far as volume relations are concerned, is therefore still the abnormal rise of the saturated vapour volume (p. 26). Since at the same time a contraction of the liquid occurs the sharpest test would be the quotient of the vapour and liquid volumes, as compared with the constant value deduced (p. 25) from the law of correspondence.

B. Additive and Constitutive Relations.

1. *Volume at the Absolute Zero.*

The colligative relations, depending directly on the number of molecules, thus appear at extreme dilution in the form of Avogadro's law and the laws of gases, and may, by means of more or less rationally based empirical rules, be followed from gases to a certain extent as far as the critical temperature, and thence into liquids, down even to the absolute zero.

In dealing with the additive relations of volume we shall reverse this order and start from the absolute zero, remembering that according to molecular mechanical conceptions at that temperature the space between the molecules is reduced as far as possible, and consequently the volume of the whole comes closest to the sum of the volumes of the parts.

With reference, however, to the additive relations in question, there is one general remark that must first be made. Strictly additive behaviour is only to be expected

either of properties which are independent of surroundings, such as mass, or under such circumstances that the influence of surroundings is excluded, as by the sufficient separation of the components which occurs in mixtures of solids, and on extreme dilution. In a chemical compound, since this separation is excluded in the case of the atoms, and is only possible with regard to the molecules, strict additivity in the relations of volume is not to be expected, and actually is not found; still the character of a mixture is retained so far as more or less approximate additive relations exist, and the deviation may in part be referred to the relative influence of the atoms, i.e. to constitutive influences, in a more or less definite manner.

Since the data which allow of judging of additive relations at the absolute zero are scanty we will first make use of the critical volume for this purpose, since according to p. 30, that is about four times the volume at the absolute zero.

2. *The Critical Volume.*

The most direct way of testing additive relations is obviously to determine the critical volumes of the elements and compare with those of compounds, as e. g.

Oxygen . . . $D_k = 0.65$ $V_k = \dfrac{16}{0.61} = 25$

Nitrogen . . $D_k = 0.37$ $V_k = \dfrac{14}{0.37} = 38$

Nitrous oxide . $D_k = 0.41$ $V_k = \dfrac{44}{0.41} = 107 \ (2 \times 38 + 25 = 101)$.

For want of material we are reduced to the indirect way, and so find that isomers have nearly the same density, and therefore molecular volume, whilst the same difference of composition is associated with nearly the same difference in molecular volume: hence conclusions may be drawn as to the volumes of the elements, as appears from the following data:

			Volume difference for CH_2
HCO_2CH_3 . . .	171		
$HCO_2C_2H_5$ . . .	228 ⎫		
$H_3CCO_2CH_3$ . . .	227 ⎬ 227·5		56·5
$HCO_2C_3H_7$ . . .	284 ⎫		
$H_3CCO_2C_2H_5$ . .	285 ⎬ 283·3		55·8
$H_5C_2CO_2CH_3$ . .	281 ⎭		
$H_3CCO_2C_3H_7$ . .	343 ⎫		
$H_5C_2CO_2C_2H_5$ . .	343 ⎬ 340·7		57·4
$H_7C_3CO_2CH_3$ . . .	339		
Methyl isobutyrate	337 ⎭		

Now making use of the critical volume of normal pentane C_5H_{12}, which is 307·2, we get

$$H_2 = C_5H_{12} - 5CH_2 = 307 \cdot 2 - 5 \times 56 \cdot 6 = 24 \cdot 2,$$

and $$C = CH_2 - H_2 = 32 \cdot 4;$$

which then leads to the value 29 for oxygen, not very different from that stated above.

Here it must be remembered that where the critical data show abnormalities, as for acetic acid, apparently on account of the formation of double molecules, the above relation also ceases to be true. The molecular volume of acetic acid at the critical point is

$$\frac{60}{0 \cdot 4065} = 147 \cdot 6,$$

i. e. far removed from that of the isomeric methyl formate 171.

3. Volume at the Boiling Point.

Since the molecular volumes at the critical point show additive properties, so also do the volumes at corresponding temperatures, since these are equal fractions of the critical temperatures, and therefore correspond to equal fractions of the critical volumes. Thus the additivity existing in the critical state leads to that discovered by Kopp for molecular volumes at the boiling point, for the boiling points are—on account of the approximate equality of

critical pressures—roughly corresponding temperatures [1], as may be seen from the following :—

Substance	Abs. crit. temp. (T_k)	Abs. b. p. (T_b)	$\dfrac{T_b}{T_k}$
Ether	467	308	0·66
Ethyl acetate	523	346	0·66
Ethylene chloride . . .	561	357	0·64
Alcohol	516	351	0·68
Benzene	562	353	0·63
Hydrochloric acid . . .	325	238	0·73
Oxygen	155	92	0·60
Carbon disulphide . . .	545	319	0·59
Ammonia	404	234	0·58
Ethylene	282	163	0·58
Methane	191	109	0·57
Sulphuretted hydrogen .	373	211	0·57
Nitrous oxide	309	183	0·59
Stannic chloride	592	387	0·65
Water	637	373	0·59
Acetic acid	595	391	0·66

From this point of view it was a fortunate idea of Kopp (1855) to compare molecular volumes at the boiling point. It appeared on the whole that these might be regarded as the sum of values peculiar to each element. With the assumption of the following atomic volumes—

C	O	H	Cl	Br	I	S
11	12·2	5·5	22·8	27·8	37·5	22·6

the molecular volume (M_v), and therefore the density at the boiling point, is roughly calculable from the molecular weight (M_g), as e. g. for acetone (C_3H_6O)—

$$M_v = 3 \times 11 + 6 \times 5 \cdot 5 + 12 \cdot 2 = 78 \cdot 2,$$
$$M_g = 3 \times 12 + 6 \quad\quad + 16 \quad = 58 ;$$

the density at the boiling point ($56 \cdot 5°$) should therefore be $\dfrac{58}{78 \cdot 2} = 0 \cdot 742$, whilst $0 \cdot 75$ is the observed value.

A striking confirmation of the values thus calculated from organic compounds is the following :

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[1] Guldberg, *Zeitschr. f. Phys. Chem.* 5. 376.

The calculated atomic volume of chlorine and bromine

$$A_v = 22 \cdot 8 \quad \text{and} \quad 27 \cdot 8,$$

for $\qquad A_g = 35 \cdot 45 \quad \text{,,} \quad 79 \cdot 96$

leads to the densities

$$\frac{35 \cdot 45}{22 \cdot 8} = 1 \cdot 55 \quad \text{and} \quad \frac{79 \cdot 96}{27 \cdot 8} = 2 \cdot 88,$$

whilst $\qquad\qquad 1 \cdot 56 \text{ and } 2 \cdot 96$

at the boiling point have been observed[1].

On the other hand discrepancies occur which were partly noticed by Kopp himself and depend primarily on the constitution.

A so-called double bond of oxygen requires a larger volume than a single bond: thus in methyl alcohol H_3C-O-H if we subtract from $M_v = 42 \cdot 6$, the values for carbon and hydrogen, $11 + 4 \times 5 \cdot 5 = 33$, there remains $9 \cdot 6$, whilst in aldehyde $H_3CC{\displaystyle {O \atop H}}$, $M_v = 56 \cdot 9$, and deducting $22 + 4 \times 5 \cdot 5 = 44$, there remains $12 \cdot 9$.

There is a second limitation; even without a change in the linkage small differences in constitution lead to somewhat different volumes (Städel), as may be seen from the following data on molecular volumes:

$CH_3CCl_3(74 \cdot 1°)$	108	$CHClBrCH_3(82 \cdot 7°)$	96.5
$CH_2ClCHCl_2(113 \cdot 7°)$	102.8	$CH_2BrCH_2Cl(107°)$	88

These differences cannot be accounted for by the fact that the boiling point is chosen instead of the critical point, for even at the latter isomers are not strictly of the same density; e. g. the difference CH_2 does not always correspond to the same differences in molecular volumes

$HCOOCH_3$	171 $\Big\}$ 57	H_3COH	118 $\Big\}$ 49
$HCOOC_2H_5$	228	H_5C_2OH	167

the final result is therefore that the molecular volume is certainly not a simple additive quantity, as according to p. 34, was to be expected.

[1] *Berl. Ber.* 31. 2762.

4. *Volume at Ordinary Temperatures.*

The unsatisfactory conclusion arrived at in comparing molecular volumes at the boiling point has led to the abandonment of Kopp's fundamental idea, and Horstmann[1] in particular has carried out a simple comparison at ordinary temperatures or at 0°.

As under these circumstances the densities of compounds with fairly high critical temperatures are about three times the critical densities, additive relations are suggested :

Substance	Critical density (D_k)	Density at 0° (D)	$\dfrac{D}{D_k}$
C_6H_6	0·304	0 90	2·96
C_6H_5F	0·354	1·047	2·96
C_6H_5Cl	0·367	1·128	3·08
CH_3OH	0·277	0·822	2·96
$(C_2H_5)_2O$	0·263	0·736	2·80
CH_3CO_2H . . .	0·352	1·080	3·07
CCl_4	0·556	1·632	2·94
$SnCl_2$	0·742	2·279	3·08
C_6H_{14}	0·234	0·677	2·89
Methyl formate .	0·349	1·000	2·87
Methyl butyrate .	0·302	0·911	3·02

but these fulfil the equation

$$M_v = \Sigma A_v,$$

even less accurately than at the boiling point[2].

This is to be expected *a priori*, since the remark that the volume at 0° is one-third of the critical volume is obviously not even approximately true for bodies whose critical temperatures are in the neighbourhood of 0°.   If only for that reason, comparison at the boiling point is to be preferred in principle.

Further, on directly testing the additivity, negative values are often obtained for the atomic volume.   As an example of this we may take the molecular volumes of the paraffins at 0° :

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[1] Graham-Otto, 1893, vol. i ; Collection of data on the subject by Horstmann.

[2] Mathias, *Journ. de Phys.*

C_4H_{10}	C_6H_{14}	C_7H_{16}	C_8H_{18}	C_9H_{20}	$C_{11}H_{24}$	$C_{16}H_{34}$
96·5	127·2	142·5	158·3	174·3	206	286·2
$CH_2 =$ 15·3		15·3	15·8	16	15·9	16

the difference for CH_2 is therefore fairly constant at 15·8. But using this value we get

$$H_2 = C_4H_{10} - 4\,CH_2 = 96·5 - 63·2 = 33·3,$$

and consequently a negative space occupied by carbon

$$C = CH_2 - H_2 = 15·8 - 33·3 = -17·5,$$

which can only be avoided by allowing very considerable weight to the constitutive influences.

These and similar points are explained when we consider that the ratio of the volume at ordinary temperatures to that at the absolute zero—and it is that to which additive relations refer in the first place—is not the same as for corresponding temperatures. In the latter case a very close approximation to proportionality with the volume V_0 at the absolute zero is to be expected, so that the volumes in question may be directly compared. But there exists the relation

$$V_0 = V_{273} - k,$$

or in words the volume V_{273} at 0° exceeds that at the absolute zero by a fixed amount k. According to the law of rectilinear diameter, remembering that the volume at the absolute zero is one-fourth of the critical volume, this becomes for bodies with high critical temperatures

$$k = \frac{273\,V_{273}}{2\,T_k}.$$

5. *The Space occupied by Matter, and the Intermolecular Space.*

We have so far restricted ourselves to spatial relations that can be dealt with empirically, and by introducing the volume at the absolute zero have avoided the distinction of the entire volume into one part occupied by matter and another which is not. This point of view is that of the

historical development of the subject. It started from the assumption made in the characteristic equation of a space or sphere of action occupied by matter, but then took the form of certain empirical rules as to the total volume, and the survey thus obtained takes in the colligative relations in their complete extent from the greatest dilution in ideal gases to the greatest density at the absolute zero.

Since, however, the additive method does not give clear results when the total volume is alone taken into consideration, it seems desirable, in accordance with the molecular mechanical view, to try the hypothesis of space partly filled with matter, and partly not, although direct experimental confirmation is then no longer possible on account of the assumption involved not being accessible to experiment.

It is Traube[1] in particular who has taken this view, dividing the total volume into the interspace or co-volume k and the true molecular volume, and regarding the latter as of an additive or partly constitutive nature; hence

$$M_v = \Sigma A_v + k.$$

It is next assumed that k is constant (25·9 at 15°), which cannot be either proved or disproved, since the co-volume is not directly measurable, but which may be brought into accordance with the facts by the additive relations arising if a sufficient number of constitutive influences are allowed for. For the hydrocarbons[2] at 15° the result is

$$M_v = 25 \cdot 9 + \Sigma A_v - (8 \cdot 1 R + 13 \cdot 2 B + 1 \cdot 7 q + 3 \cdot 4 r),$$

where A_v has the values 9·9 and 3·1 for the carbon and hydrogen atoms respectively, and R, B, q, r, are the number of hexamethylene and benzene rings, and double or triple linkages.

[1] Ahrens, *Sammlung von Vorträgen*, 1899 ; Biltz, *Praxis der Molekulargewichtsbestimmung*, 1898, p. 154 ; Nasini, *Gazz. Chim. ital.* 27 (ii), p. 533.
[2] *Berl. Ber.* 28. 2926.

Thus for amylene

$$CH_3 - CH_2 - CH_2 - CH = CH_2,$$
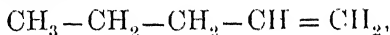
$M_v = 5 \times 9 \cdot 9 + 10 \times 3 \cdot 1 - 1 \cdot 7 + 25 \cdot 9 = 104 \cdot 7$ (obs. $105 \cdot 1$):
this equation may be used to determine molecular weights
if there are sufficient data for the constitution, and conse-
quently for the part played by constitutive influences.

Thus if we have a hydrocarbon whose analysis gives

$$(CH_2)_n$$

with a density $0 \cdot 7977$ at 15° we get

$$M_c = \frac{14 n}{0 \cdot 7977},$$

and on the other hand

$$M_v = 25 \cdot 9 + 16 \cdot 1\, n - 1 \cdot 7 \text{ or } 25 \cdot 9 + 16 \cdot 1\, n - 8 \cdot 1,$$

since the hydrocarbon may contain either a double linkage
or a hexamethylene ring. If the latter is excluded on other
grounds, then

$$\frac{14 n}{0 \cdot 7977} = 25 \cdot 9 + 16 \cdot 1\, n - 1 \cdot 7,$$

whence $\qquad n = 16 \cdot 7$, or probably 17,

which indicates that the hydrocarbon is heptadecylene.

Since, however, this rule is purely empirical, it must be
handled with the greatest discretion, particularly with
regard to molecular doubling in liquids, since, according to
p. 26, it is not probable that this exercises a large influence
on the volume of the liquid.

6. *The Volume in Solution.*

In order to extend the range of comparison, and so bring
out better the additive and constitutive relations, the volume
of a dissolved body has often been considered. In recent
times this has attained a higher interest in the case of
dilute solutions, on account of the insight which the new
theory of solutions gives as to the state of dissolved bodies.
Two chief points must be attended to in this connexion if
we first deal with aqueous solutions. In the first place,
the formation of double molecules, which (p. 26) occurs
in hydroxylic bodies, especially in formic and acetic acids,

methyl and ethyl alcohols, is prevented by solution in water, consequently the abnormal density so caused in the bodies mentioned vanishes in aqueous solution. In the second place, according to modern views, electrolytes, on sufficient dilution, decompose into identical parts — the ions—so that sharply additive relations of volume should show themselves.

A difficulty arises, however, in the fact that the molecular volume in solution cannot be calculated in a manner quite free from objection from the formula

$$m_v = \frac{m+n}{d} - \frac{n}{\delta};$$

where m represents the molecular weight of the dissolved substance in grams, n the weight of solvent containing it, d the density of the solution, δ that of the solvent. The difficulty lies in the density of the solvent, which is not necessarily the same in the solution as in the pure state. We will, first, however, in making calculations on the subject, leave this objection out of account, as we are doubtless justified in doing, for the case of ideal dilution.

Let us consider, first, the effect of doubling of molecules, or of so-called association, on the volume of liquids. According to p. 26, it appears that this is probably not large. With this agrees the result that the molecular volume determined as such (M_v), and the volume in dilute solution, do not differ much, whether for associated or non-associated liquids:

Substance	M_v ($15°$)	m_v ($15°$)	$\dfrac{M_v - m_v}{M_v + m_v} \times 100$
(*associated*)			
Methyl alcohol . .	40·2	38·6	2
Ethyl alcohol . .	57·9	55·1	2·5
Formic acid . . .	37·5	34·5	4·2
Acetic acid . . .	56·8	51	5·4
(*non-associated*)			
Methyl acetate . .	78·8	71·4	4·9
Ethyl acetate . .	97·1	87·8	5
Propyl formate . .	96·8	89·2	4·1
Ethyl propionate .	113·9	104.4	4·3

The change due to taking the volume in solution into account is thus in all cases a small one; still, it gives a somewhat better result[1] from the fact that similar changes in composition are accompanied by somewhat more corresponding changes in volume. Anyhow, the gain is not very great, since for oxygen, e.g. it is necessary to assume four volumes, according as it appears in the form of carbonyl, or ether, or isolated hydroxyl-oxygen, or hydroxyl in the neighbourhood of another oxygen atom, in the carboxyl group. Taking these constitutive influences into account, an empirical formula like that on p. 40 may be developed for the volume in solution, and, like the other, may be made use of for molecular weight determinations. But there is hardly any need of this, seeing that reliable osmotic methods exist for the case in question.

Let us next discuss what has been arrived at with regard to electrolytes. Here additive relations were first discovered by Bender and Valson, but were expressed in terms of the density. Later calculations refer to the volume in solution.

The most essential fact is that whilst the volume of non-electrolytes, as shown above, varies little with the concentration, that of electrolytes varies largely[2]:

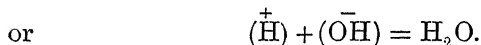| *Normality*	$NaCl$ (18°)	$\frac{1}{2} H_2SO_4$ (18°)
0·0025	—	6·93
0·005	16·39	7·94
0·05	16·37	12·77
0·1	16·57	14·05
1	17·97	16·96
5	20·9	18·52

only becoming constant when the maximum molecular conductivity is reached, as is the case for sodium chloride in $\frac{1}{20}$ normal solution, but for sulphuric acid only on much greater dilution. Strictly additive relations are only to be expected for these limiting values, and do actually occur

[1] Traube, l. c.
[2] Kohlrausch and Hallwachs, *Wied. Ann.* 53. 14 ; 56. 185.

then, so that the volume of the solution is calculable from the value for each ion obtained by measurement of a single compound.

The change of volume on dissociation into ions appears, according to these numbers, to be a diminution. This may be referred to the important fact that the formation of ions, perhaps on account of the attraction of the opposite electric charges, causes a contraction, which may in certain cases be calculated. Thus e. g. if a strong base be neutralized by a strong acid, instead of the contraction that might at first be expected, an expansion takes place, amounting, according to Ostwald, to 20·05 c.c. for one kilogram of each solution, containing a gram-molecule of acid and base respectively. In this case two ions disappear, according to the equation

$$(\overset{+}{H})(\overset{-}{NO_3}) + (\overset{+}{K})(\overset{-}{OH}) = (\overset{+}{K})(\overset{-}{NO_3}) + H_2O,$$

or
$$(\overset{+}{H}) + (\overset{-}{OH}) = H_2O.$$
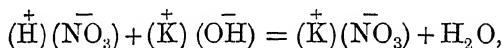
If the acid and base are weak, i. e. not dissociated whilst the salt formed is dissociated, as in the case of butyric acid and ammonia, a contraction of 18·65 c.c. occurs, here new ions are formed:

$$C_4H_8O_2 + NH_3 = (C_4\overset{-}{H_7}O_2)(\overset{+}{NH_4}).$$
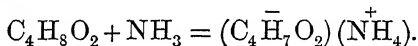
Thus the formation or disappearance of two gram-ions in about two litres of water causes a contraction or expansion of 20 c.c. on the average, or 10 c.c. for one gram-ion per litre.

§ 2. Pressure Relations.

A. Deductions from the Characteristic Equation [1].

Starting from the simple form of the characteristic equation

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT,$$

---

[1] During proof-correction the inaugural dissertation by Reinganum (Göttingen, 1899) on this subject appeared. Dieterici, *Wied. Ann.* 69. 685.

we get at once the necessary conclusion that the pressure is a linear function of the absolute temperature, when the volume is constant.

$$P = \frac{R}{V-b}\, T - \frac{a}{V^2} = cT - k.$$

In this expression k vanishes for sufficient dilution, leaving the pressure proportional to the absolute temperature, according to the limit-law of Gay-Lussac. The more general relation mentioned above is very approximately true, as is indicated, e. g. by the following numbers for pentane [1]:

Temperature	40°	60°	80°	100°	120°	160°	200°	240°	280°
Pressure	857	920	981	1040	1100	1219	1334	1451	1571 mm.
Difference		63	61	59	60	2×60	2×63	2×59	2×60 mm.

A second numerical relation between two bodies depends on the law of correspondence, and gives that at equal fractions of the critical temperatures, the saturation pressures are equal fractions of the critical pressures. In the following table are given the reduced temperatures $\dfrac{T}{T_k}$ for hexane, pentane, and benzene, at equal reduced pressures $\dfrac{P}{P_k}$:

$\dfrac{P}{P_k}$		$\dfrac{T}{T_k}$	
	C_6H_{14}	C_5H_{12}	C_6H_6
1	1	1	1
0.7372	0.959	0.957	0.957
0.4423	0 896	0.890	0.891
0.2064	0.815	0.806	0.805
0.0442	0.691	0.678	0.677

From the agreement of the values for $\dfrac{T}{T_k}$, which though not perfect is very close, it follows that with the aid of any comparison substance the vapour pressure at given temperature of any other substance is calculable, if one knows the critical temperature and pressure of the latter.

[1] Rose-Innes and Young, *Phil. Mag.* 1899, p. 353.

As an instance of this we will calculate the saturation pressure of ether at $103°$. Since here

$$T_k = 467\cdot4; \qquad P_k = 27060 \text{ mm.,}$$

we have

$$\frac{T}{T_k} = \frac{273+103}{467\cdot4} = 0\cdot805.$$

Taking benzene as comparison substance it appears from the preceding table that for

$$\frac{T}{T_k} = 0\cdot805, \qquad \frac{P}{P_k} = 0\cdot2064;$$

so that for ether

$$P = 0\cdot2064 \times 27060 = 5590 \text{ mm.}$$

According to Regnault, for ether

$$P_{100} = 4953\cdot3, \qquad P_{110} = 6214\cdot63,$$

and linear interpolation gives

$$P_{103} = 5332.$$

As a second instance we will calculate the boiling point of ether. Then

$$\frac{P}{P_k} = \frac{760}{27060} = 0\cdot0281 ;$$

whence interpolating from the data for fluor-benzene as standard substance

$\dfrac{P}{P_k}$	$\dfrac{T}{T_k}$
0.0295	0.656
0.0224	0.640

$$\frac{T}{T_k} = 0\cdot653 \text{ and } T = 0\cdot653 \times 467\cdot4 = 305$$

i. e. on the centigrade scale $305 - 273 = 32°$, whilst $35°$ is observed.

B. Empirical Relations and Molecular Weight.

Since the characteristic equation brings out insufficiently the relations between pressure and temperature, we are obliged either to restrict ourselves to direct use of the numbers for a comparison body, or to express these by

empirical relations, as was done for volumes by Mathias' law of the rectilinear diameter. The following has been suggested [1] :

$$\log \frac{P_k}{P} = f\left(\frac{T_k}{T} - 1\right),$$

which we may test by the numbers for fluor-benzene :

P P_k	T T_k	$f = \dfrac{\log. \frac{P_k}{P}}{\frac{T_k}{T} - 1}$
0·59	0·929	3·00
0·236	0·823	2·92
0·089	0·733	2·89
0·0205	0·656	2·94
0·0118	0·606	2·97
0·00059	0·480	3·05

Whilst most substances are approximately united by these relations, striking exceptions are to be noted, being found especially in those bodies which are regarded as partly or wholly double-molecular, on the ground of the osmotic methods. We must especially notice the behaviour of bodies such as ethyl alcohol, which behaves normally in the critical state (p. 22), and therefore probably possesses normal molecular weight; retaining the same in the form of saturated vapours at low temperatures, as shown by the density; but appearing as double-molecular in the liquid form on cooling, as judged by the osmotic methods.

Let us therefore compare the vapour pressure of ether—a normal liquid—with alcohol at corresponding temperatures, fluor-benzene being taken as the standard substance :

$\dfrac{T}{T_k}$	C_6H_5F	$(C_2H_5)_2O$	C_2H_5OH
1	1	0·708	1·411
0·928	1	0·804	1·253
0·822	1	0·785	0·902
0·733	1	0·761	0·681
0·639	1	0·740	0·400

The saturation pressure of ethyl alcohol thus falls off

[1] V. d. Waals, *Continuity*, p. 148.

abnormally on fall of temperature, being for $\frac{T}{T_k} = 0.639$, less than a third (0.409) of its original value (1.411), whilst that of ether is approximately constant. This, however, is the behaviour to be expected as a result of molecular doubling, since the originally monomolecular liquid then contains double-molecules, as a component, and these lower the vapour pressure. This fact obviously agrees with that already mentioned (p. 26), that saturated ethyl alcohol vapour, on cooling, occupies an abnormally great volume.

§ 3. TEMPERATURE RELATIONS.

A. The Critical Coefficient.

In what precedes we found among the critical data partly additive, partly colligative, properties. The former, as to the volume, which is quadruple the volume at the absolute zero, the latter, as to the volume compared with the theoretical volume under the critical pressure and temperature.

Starting from the empirical expression of the latter relation (p. 23),

$$\frac{P_k V_k}{T_k} = \frac{R}{3.7},$$

or

$$V_k = \frac{R}{3.7} \cdot \frac{T_k}{P_k};$$

it appears that the additive properties of the volume must also be traceable in the quotient

$$\frac{T_k}{P_k}.$$

From the theoretical relation deduced on p. 21

$$3V_k = b + \frac{RT_k}{P_k},$$

and

$$V_k = 3b,$$

we get the same result, since

$$\frac{T_k}{P_k} = \frac{8b}{R},$$

according to which the quotient $\dfrac{T_k}{P_k}$ is proportional to the volume b at the absolute zero, and accordingly like that quantity, of essentially additive nature.

This quotient $\dfrac{T_k}{P_k}$ has therefore a special meaning, and is called by Guye[1] the critical coefficient. It may be approximately obtained by addition from the following values:

C = 1·35	H = 0·57	$\overset{\shortmid}{\text{O}}$ = 0·87	$\overset{\shortparallel}{\text{O}}$ = 1·27
Cl = 2·66	N = 1·6	$\overset{\text{iii}}{\text{N}}$ = 1·86	P = 3·01

Double linkage = 0·88.   Triple linkage = 1·03.

Let us take first, as example:

Propyl formate $\text{HC}\diagup^{\text{O}}_{\diagdown \text{OC}_3\text{H}_7},$

$$4\,\text{C} + 8\,\text{H} + \overset{\shortmid}{\text{O}} + \overset{\shortparallel}{\text{O}} = 5\cdot4 + 4\cdot56 + 0\cdot87 + 1\cdot27 = 12\cdot1.$$

The experimental results are:

$$T_k = 533\cdot8 ; \qquad P_k = 42\cdot7 \text{ atm.} ;$$

so that

$$\frac{T_k}{P_k} = \frac{533\cdot8}{42\cdot7} = 12\cdot5.$$

It is of importance that here, too, we have an indication as to molecular magnitude, since, e. g., acetic acid ($\text{C}_2\text{H}_4\text{O}_2$) gives

$$\frac{T_k}{P_k} = \frac{273 + 321\cdot65}{57\cdot1} = 10\cdot4 \quad \text{observed against}$$

$$2\,\text{C} + 4\,\text{H} + \overset{\shortmid}{\text{O}} + \overset{\shortparallel}{\text{O}} = 2\cdot7 + 2\cdot28 + 0\cdot87 + 1\cdot27 = 7\cdot12 ;$$

a large deviation, which is in agreement with the fact, demonstrated on all hands, that acetic acid in the critical state is partly associated.   The formula

$$\begin{array}{ccc} \text{CH}_3 & & \text{CH}_3 \\ | & & | \\ \text{HO—C}&\diagup^{\text{O}}_{\diagdown \text{O}}&\text{C—OH} \end{array}$$
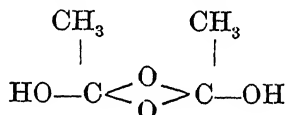
would lead to

$$4\,\text{H} + 8\,\text{H} + 4\overset{\shortmid}{\text{O}} = 5\cdot4 + 4\cdot56 + 3\cdot48 = 13\cdot44.$$

[1] *Thèses*, 1891.

An equally important application is to the case of phosphonium chloride PH_4Cl, whose critical temperature $50°·5$, lies only a few degrees above the melting point.   Here

$$\frac{T_k}{P_k} = \frac{273 + 50·5}{80} = 4,$$

whilst

$$P + 4H + Cl = 3·01 + 2·28 + 2·66 = 7·95.$$

It is natural to suggest, as a reason for the abnormally small critical coefficient, a dissociation into PH_3 and HCl. From which again it may be concluded, with some probability, that the melting of phosphonium chloride is not a fusion in the strict sense, but a transition into a liquid mixture of the components.

B. Boiling Point.

1. *Additive Relations.*

The additive relations found in the critical coefficient, are to be expected also in the quotient of temperature by pressure for corresponding temperatures ; for then the temperatures are equal fractions of the critical

$$T = aT_k,$$

and the pressures equal fractions of the critical pressures

$$P = \beta P_k,$$

so that

$$\frac{T}{P} = \frac{aT_k}{\beta P_k} = \gamma \frac{T_k}{P_k}.$$

The relations observed in the critical coefficients consequently appear also in the quotients $\frac{T}{P}$ for corresponding temperatures.   Remembering, then, that according to p. 36 the boiling points are approximately corresponding temperatures, and that here P is unity, additive relations are to be expected in the boiling points, as Kopp, in particular, pointed out.   These additive relations may be referred to those, also observed by Kopp, in the molecular volume at

the boiling point[1]. In the first place, at corresponding temperatures the ratio between volumes of liquid and vapour is constant, if no molecular association occurs.

$$\frac{V_d}{V_l} = k.$$

If further the saturated vapour is dilute enough, then V standing for the molecular volume, we have

$$V_d = \frac{2T}{AP},$$

so that

$$T = 2\,k\,A\,P\,V_l.$$

The assumption that P is one atmosphere for corresponding temperatures, makes kPA constant, and therefore the boiling point T proportional to the molecular volume V_l.

The radical test of this, by means of the elements themselves, is partly possible with the data in existence. Thus :

Boiling point of hydrogen	.	$-238°$C.	$= 35°$ abs.[2]	(H	$=$	17)
,, ,, oxygen	.	-181	,, 91 ,,	(O	$=$	46)
,, ,, nitrogen	.	-194	,, 79 ,,	(N	$=$	39)
,, ,, chlorine	.	-33	,, 239 ,,	(Cl		120)
,, ,, bromine	.	63	,, 336 ,,	(Br	$=$	168)
,, ,, iodine	. .	184	,, 457 ,,	(I	$=$	229)
,, ,, phosphorus		288	,, 561 ,,	(P	$=$	140)
,, ,, mercury	.	357	,, 630 ,,	(Hg	$=$	630)
,, ,, sulphur	.	448	,, 721 ,,	(S	$=$	90)

Simple binary compounds :

Water	. . . . . .	$100°$ calc.	$34 + 46 - 273 =$	-208
Ammonia	. . . .	-39	,, $51 + 39 - 273 =$	-183
Nitric oxide	. . . .	-154	,, $46 + 39 - 273 =$	-188
Hydrochloric acid	. .	-84	,, $17 + 120 - 273 =$	-130
Hydrobromic acid	. .	-65	,, $168 + 17 - 273 =$	-88
ClO_2	. . . . . .	10	,, $120 + 92 - 273 =$	-61
Cl_2O	. . . . . .	20	,, $240 + 46 - 273 =$	$+13$
HI	. . . .	-34	,, $229 + 17 - 273 -$	-27
PCl_3	. . . . . .	78	,, $140 + 360 - 273 =$	$+227$
$HgCl_2$	. . . . . .	307	,, $630 + 240 - 273 =$	$+597$
SH_2	. . . . . .	-62	,, $90 + 35 - 273 =$	-148

[1] Orme Masson, *Zeitschr. f. Phys. Chem.* 6. 595.
[2] *Centralblatt*, 1899, 1. 912.

There is therefore no question of strictly additive relations, which is not surprising, since the boiling points are not corresponding temperatures—the critical pressures vary widely (15 atm. for hydrogen, 200 for water)—so that we must give up Kopp's attempt to find indirectly from the compounds a number for each element, and to calculate the boiling point of compounds by addition of these. Still the additive character is not so completely hidden, but that certain important rules can be deduced from it: we will consider these next.

(*a*) *Equal Boiling Points of Isomers.*

Equality in the boiling points of isomers is an immediate consequence of additivity. It is often found in practice. We may take as example the isomers of the formula $C_9H_{18}O_2$:[1]

Methyl octoate	. . .	192.9°	Amyl butyrate	. . .	184.8'
Ethyl heptoate	. . .	187.1	Heptyl acetate	. . .	191.3
Propyl hexoate	. . .	185.5	Octyl formate	. . .	198.1
Butyl pentoate	. . .	185.8			

(*b*) *Increase of Boiling Point with Molecular Weight.*

If the compounds are not isomeric, but polymeric, or more generally if the one molecule is, according to the kind and number of its atoms, larger than the other, then mostly the higher boiling point is found for the larger molecule, in accordance with the additive character of that property. Consider the compounds of nitrogen and oxygen.

The smallest—diatomic—molecules correspond to the lowest boiling points, and to gases that were long known as permanent.

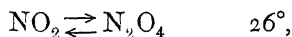$$O_2 - 181° \qquad N_2 - 194° \qquad NO - 154°.$$
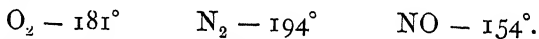
The triatomic boil a good deal higher:

$$O_3 - 106° \qquad N_2O - 87°,$$

---

[1] For this and the following the collection in Graham-Otto, 1898, by Marckwald (1st vol., part 2) has mostly been used.

then follows

$$NO_2 \rightleftarrows N_2O_4 \qquad 26°,$$

and finally $\qquad\qquad N_2O_5,$

solid at ordinary temperatures and decomposed above 50°.

(c) *Equal Differences in Boiling Point for Equal Differences in Composition.*

It is often found that equal differences of composition produce equal differences in boiling point, as is generally the case among homologous bodies such as those differing by CH_2. Taking the esters as examples:

Methyl octoate	192.9°		
,, heptoate	172.1	Difference	20.8
,, hexoate	149.6	,,	22.5
,, pentoate	127.3	,,	22.3
,, butyrate	102.3	,,	25
,, propionate	79.5	,,	22.8
,, acetate	57.3	,,	22.2
,, formate	32.5	,,	24.8

The effect of CH_2 is to cause a difference of from 20.8° to 25° or, as usually, not far from 20°.

(d) *Compounds of more or less Volatile Elements.*

On replacing one element in a compound by another the relative volatility of the two often causes a change in boiling point, e. g.

H_2 $- 238°$ F_2 $- 185°$ Cl_2 $- 33°$ Br_2 $59°$ I_2 $184°$
C_6H_6 $80.4°$ C_6H_5F $85°$ C_6H_5Cl $132°$ C_6H_5Br $155°$ C_6H_5I $190°$

In connexion with this is the fact that though increase in the size of the molecules causes in general a rise of boiling point, addition of the very volatile hydrogen causes hardly any changes, or sometimes a fall:

Benzene (C_6H_6) 80.4°   Hexamethylene (C_6H_{12}) 70°.

(e) *Molecular Weight and Boiling Point.*

It follows from the additive character that an abnormal increase of molecular weight is of the greatest influence on

the boiling point. There are striking facts in this connexion which give indications with regard to molecular weight [1].

Let us take first a body like acetic acid, which is probably in part associated even at the critical point. The critical coefficient is then (p. 49) abnormally high, and accordingly also the boiling point. To this must be referred most of the difference between the boiling point of acetic acid ($118°$) and that of the isomeric methyl formate ($32.5°$) which is apparently not associated. Thus the boiling point of acetic acid lies halfway between the latter value and that which would be due to the doubled molecule $C_4H_8O_4$, and which would presumably not be very different from that ($164.2°$) of methyl oxalate ($C_4H_6O_4$).

Bodies which, like methyl alcohol, behave normally at the critical point, but become associated in the liquid form at lower temperatures, show according to p. 47 an abnormal fall in vapour pressure and therefore also a raised boiling point. This may be seen in the case of methyl alcohol (boiling point $66°$) since $(CH_3)_2O$ boils at $-23°$ and the lower homologue CH_4O would be expected to have the boiling point $-43°$. Water too boils at far too high a temperature ($100°$) for a compound H_2O since this, regarded as a lower homologue of methyl oxide, should boil at $-63''$.

It may be repeated that the cryoscopic methods indicate association in the case of methyl alcohol and water, as of most hydroxylic compounds.

Finally in the case of carbon which is hardly at all volatile, it appears that there must be a very striking difference between the molecular constitutions C and C_2, since the volatility of C_2 should be about that of a hydrocarbon with two atoms of carbon.

2. *Constitutive Influences.*

It is the more important to discuss the play of constitutive influences, since according to p. 52 the additive

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[1] Vernon, *Chem. News*, 64. 54 ; Nernst, *Theoretische Chemie*, 312.

relations at the boiling point are the less marked, on account of the divergence of boiling points from being corresponding temperatures: so that along side of the rules depending on the additive character, others arise depending on constitution, and therefore referring in the first place to isomers.

(a) *Rise of Boiling Point under the Influence of Strong Affinities.*

A leading empirical rule is, that compounds formed under the action of strong affinities, and so with a great evolution of heat, have high boiling points, and vice versa.

This fact appears even in the table on p. 51 since only the compounds formed under the action of weak affinities, such as Cl_2O, NO, and HI, show boiling points in fair accord with those calculated by addition from the elements, whilst in other cases, such as hydrochloric acid and ammonia, the boiling point often lies 100° higher.

Very striking instances of this may be found, such as the involatility of potassium chloride as compared with the relative volatility of its components, and on the other hand the volatility of a compound with weak affinities, $Ni(CO)_4$ despite the involatility of one of its components.

The view suggests itself that this rise of boiling point caused by affinity implies that in the expression

$$P = \frac{RT}{V-b} - \frac{a}{V^2},$$

b is small, and a large, and consequently P small.

Accumulation of Negative Atoms or Groups. With the general rule mentioned above may be associated one as to the influence on the boiling point of the accumulation of negative groups, or atoms, such as will be described more exactly later, the halogens, oxy-groups, cyanogen and the like. We have e. g.

H_2CClH_2CCl, boiling point 84°, and
H_3CCHCl_2 „ 58°, Diff. +26°.
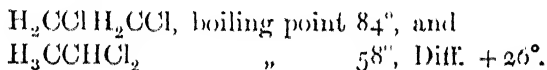
Here is to be noted also :

(a) When one negative group replaces another the influence is about the same in different compounds :

e. g. if chlorine be replaced by bromine the boiling point is raised, usually by 22°.

(β) When one positive group replaces another the same is true, the replacement of H by CH_3 being the most frequent instance.

(γ) If a negative group replaces a positive one, e. g. chlorine, hydrogen, the influence is quite different according as there are already negative groups present or not.   In the former case [1] i. e. on introducing

$$\begin{array}{lll}
\text{Cl in } CH_3 & \text{the rise averages} & 66° \\
\text{Cl in } CH_2Cl & \text{,,} \qquad \text{,,} & 39° \\
\text{Cl in } CHCl_2 & \text{,,} \qquad \text{,,} & 13°
\end{array}$$

A very striking example due to the researches of Henry on chlorinated acetonitril is

$$NCCH_3\ 81° \qquad NCCH_2Cl\ 123° \qquad NCCHCl_2\ 112° \qquad NCCCl_3\ 83°$$
$$+\ 42° \qquad\qquad\qquad -\ 11° \qquad\qquad -\ 29°$$

Here then the introduction of chlorine, instead of hydrogen, causes a fall in the boiling point.

(b) *Influence of Molecular Symmetry.*

Besides the action of strong affinities the symmetry of the molecule is of influence, and in general depresses the boiling point [2].   This is noticeable in the list of isomeric esters given on p. 52, since the boiling point is highest for the most unequal division of the carbon atoms :

Methyl octoate 192·9°   Octyl formate 198·1°, whilst there is a minimum for

Amyl butyrate 184·8°.

This is equally true of the simple hydrocarbons :

$$\begin{array}{lll}
CH_3CH_2CH_2CH_2CH_3 & \ldots \ldots & 38° \\
(CH_3)_2CHCH_2CH_3 & \ldots \ldots & 30° \\
(CH_3)_4C & \ldots \ldots & 9·5°
\end{array}$$

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[1] Van 't Hoff, *Ansichten über Org. Chem.* 2. 20, 22, 26.

[2] Earp. *Phil. Mag.* (5) 35. 458, 1893 ; Nernst, *Theoretische Chemie*, 1898, 314.

Similar results have been noted for alcohols, ethers, amines, mercaptans, haloids, in short for all compounds of the formula

$$C_n H_{2n+1} X$$

that is, the boiling point is lowest when the group X occupies the most central position.

§ 4. CALORIMETRIC RELATIONS.

We will bring together under this heading all that refers to the quantities of heat absorbed or given out in physical changes. Of these the latent heat of evaporation will be taken first, because it can be brought into connexion with the characteristic equation; next comes the specific heat, with regard to which the connexion with theory is not so far advanced.

A. Latent Heat of Evaporation.

In applying the second law of thermodynamics in the well-known form (Part I, p. 19)

$$A\,V dP = q\frac{dT}{T}$$

to the act of evaporation, the increase of volume V, when the liquid volume is small, as is the case for small values of P, may be set, as a first approximation, equal to the volume of the vapour itself ; then from the equation

$$APV = 2T$$

we get

$$\frac{dP}{P} = q\frac{dT}{2T^2},$$

in which q refers to the molecular quantity. The law of corresponding states may be applied to this relation when transformed into

$$\frac{dP}{P} : \frac{dT}{2T} = \frac{q}{T}.$$

The first term is obviously constant for corresponding states. If e. g. two substances have critical pressures and

temperatures $P'_k\ P''_k$ and $T'_k\ T''_k$, then for two corresponding temperatures near together we have the following states:

For the first body

$$a P'_k \quad \text{and} \quad \beta T'_k$$
$$(a + d a) P'_k \quad \text{,,} \quad (\beta + d \beta) T'_k,$$

and for the second, corresponding:

$$a P''_k \quad \text{and} \quad \beta T''_k$$
$$(a + d a) P''_k \quad \text{,,} \quad (\beta + d \beta) T''_k,$$

so that in each case

$$\frac{dP}{P} : \frac{dT}{T} = \frac{d a}{a} : \frac{d \beta}{\beta} \ .$$

In so far as boiling points are corresponding temperatures, according to Guldberg (p. 36) we have for them

$$\frac{q}{T} = \text{constant},$$

a rule long since given by Deprez and Trouton in the form, that the quotient of the molecular latent heat by the absolute boiling point is constant.

The following numbers may serve as confirmation of this:

Substance	$W = \dfrac{q}{M}$	$T - 273$	$\dfrac{q}{T}$
Benzene	94·4	80·2	20·85
Methyl formate	110·1	31·8	21·68
Carbon disulphide	86·7	46	20·32
Phosphorous chloride . . .	51·4	76	20·07
Stannic chloride	30·5	113·9	20·49
Ethylene bromide	43·8	131·5	20 38
Methyl iodide	46·1	43·8	20·66
Carbon tetrachloride . . .	46·4	76·7	20 42
Diethylamine	91	56	20·07

The deviations for abnormal molecular weight are important.

If, as with acetic acid, the saturated vapour is of abnormally high molecular weight, the relation

$$A P V = 2 T$$

does not hold for the normal molecular weight ($C_2H_4O_2 = 60$), but for a higher value (about 97 according to Part II, p. 48), so that q must be for that quantity also. If that is not the case, the quotient $\frac{q}{T}$ becomes abnormally small, thus:

$$W = 97 \qquad T - 273 = 118 \cdot 5 \qquad \frac{q}{T} = 14 \cdot 87.$$

If, as for ethyl alcohol, the vapour is normal, but the liquid partly associated, then q is too large:

$$W = 216 \cdot 5 \qquad T - 273 = 78 \cdot 2 \qquad \frac{q}{T} = 28,$$

which might be expected for several reasons. On the one hand, in addition to the latent heat, there is an absorption of heat in breaking up the double molecules, by which q becomes abnormally large. On the other hand, according to p. 47, formation of double molecules causes an abnormally rapid fall in the saturation pressure (dP) which according to the thermodynamic relation of p. 57, necessarily implies a high value of q.

Since the molecular elevation of the boiling point t stands in relation with the latent heat W (Part II, p. 56), for:

$$t = \frac{0 \cdot 0198\, T^2}{W} = \frac{0 \cdot 0198\, T^2 M}{q} = \frac{0 \cdot 0198\, TM}{20 \cdot 63} = 0 \cdot 00096\, TM,$$

the molecular elevation of the boiling point also throws light on the molecular magnitude M of the solvent. Normal solvents give actually values for $\frac{t}{TM}$ close to $0 \cdot 00096$; carbon disulphide $0 \cdot 00096$, benzene $0 \cdot 00095$. For acetic acid, if M be taken as 60, we get the abnormally high value $0 \cdot 00108$: for water and ethyl alcohol $0 \cdot 00076$ and $0 \cdot 00072$ respectively, abnormally small, as is to be expected from the foregoing argument [1].

It may be added that deviation of the latent heat of evaporation from Trouton's rule is one of the most com-

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[1] Herz, *Molekulargrösse der Körper* (Ahrens, *Sammlung*), 1899.

plete indications for judging of the extent of molecular association, since the latter is merely proportional in amount to the deviation.

Finally it is to be noted that since $\frac{q}{T}$ at corresponding temperatures is constant, and T then the same fraction of the critical temperature, q at the temperatures in question must be proportional to the critical temperature. Here also a special interest attaches to the absolute zero as being both a corresponding and a constant temperature, at which molecular movement ceases. The molecular latent heat of evaporation, which is then nothing else than the work done against internal attractions in expansion to infinity should be proportional to the critical temperature, a conclusion to which the arguments of pp. 21 and 63 also lead.

B. Specific Heat.

When heat is communicated to a body which does not change its state of aggregation, in general both its volume and temperature change. The former involves a consumption of heat in the performance of both internal and external work, so that the whole amount is divided into three parts, each of which may be considered separately. It is convenient to begin with gases at extreme dilution, or so-called perfect gases, since there the internal work of expansion is zero.

1. *Specific Heat of Perfect Gases.*

The heat, which on warming a perfect gas, serves only for rise of temperature and for performing external work, may be separated into these parts both experimentally and by calculation.

Experimentally by preventing any change of volume in a calorimetric determination, so as to measure the specific heat at constant volume. This we shall denote by C_v referring to the kilogram-molecule.

By calculation, by deducting from the specific heat under inconstant volume the heat converted into external work. The calculation is very simple when the specific heat is that at constant pressure (C_p per kilogram-molecule). The external work per 1° is then

$$\frac{d\,APV}{dT} = \frac{d\,2\,T}{dT} = 2.$$

In accordance with this we have these results :

	C_p	C_v	$C_p - C_v$
O_2	6·96	4·96	2
N_2	6·83	4·83	2
$C_{10}H_{16}$	68·8	66·8	2

Thus the heat C_v serving for pure rise of temperature, kinetically considered, causes two changes: in the molecule, the velocity as measured by that of its centre of gravity, is increased, and the external pressure consequently raised; in the atoms also the movements become more rapid, but in consequence of this the relative distances of the atoms are increased, anticipating chemical decomposition. Here again we may separate the first factor by choosing a monatomic gas; for in that case the specific heat may be calculated directly from the kinetic theory.

According to the foregoing (Part II, p. 18) we have

$$PV = \tfrac{1}{3}\,NMC^2,$$

where N is the number of molecules in volume V (in cubic metres), M their mass, C their velocity : so that the kinetic energy of the molecular movement

$$\tfrac{1}{2}\,NMC^2 = \tfrac{3}{2}\,PV,$$

and if NM is the mass of a kilogram-molecule the work done in calories is

$$\tfrac{3}{2}\,APV = 3\,T.$$

Hence for any gas the energy of molecular movement at 0° is $3 \times 273 = 819$ calories.

The specific heat at constant volume is accordingly

$$C_v = \frac{d\,3T}{dT} = 3,$$

and at constant pressure

$$C_p = C_v + 2 = 5.$$

For mercury, it is well known, these numbers have been confirmed, and are now regarded as the test of a monatomic gas. For if the gas were polyatomic both C_v and C_p would be increased by the calories required for accelerating the atomic movements and for separating the atoms, and we should have

$$C_v = 3 + a \qquad\qquad C_p = 5 + a.$$

And accordingly, as was stated above, C_v and C_p are always found greater than 3 and 5 for polyatomic gases. On the other hand the ratio

$$\frac{C_p}{C_v} = \frac{5 + a}{3 + a}$$

can be determined from the velocity of sound, and was found by Kundt and Warburg for mercury, in accordance with theory, to be

$$\frac{C_p}{C_v} = \frac{5}{3} = 1 \cdot 67;$$

whilst for other gases

$$\frac{C_p}{C_v} = \frac{5 + a}{3 + a} < 1 \cdot 67 > 1,$$

as e. g. in the case of oxygen O_2

$$C_p : C_v = 6 \cdot 96 : 4 \cdot 96 = 1 \cdot 4.$$

The criterion has lately been of great value as applied to the gases discovered by Ramsay, Argon, Helium, Neon, Metargon, and Krypton, all of which are found to be monatomic.

There is another test as well. The specific heat is independent of temperature for the monatomic gases, whilst for polyatomic, according to Le Chatelier[1], it is made up of

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[1] *Zeitschr. f. Phys. Chem.* **1**. 456.

a part independent of temperature, and a part depending on the latter, and representing the increase in molecular and atomic movements:

$$C_p = 6 \cdot 5 + bT.$$

The co-efficient b increases with the compositeness of the molecule, thus:

for $\quad$ H_2, N_2, O_2, CO $\qquad b = 0 \cdot 001$,

for $\quad$ $(C_2H_5)_2O$ $\qquad\quad b = 0 \cdot 0738$,

in accordance with the high molecular specific heat of such compound gases.

Finally, it must be mentioned that chlorine, bromine, and iodine have abnormally high specific heats

$$C_p = 8 \cdot 81 \qquad 8 \cdot 88 \qquad 8 \cdot 53,$$

which is perhaps connected with the dissociation occurring in these gases at high temperatures, and indicates a preliminary loosening of the atoms.

2. *Specific Heat of Liquids.*

Whilst in gases, either at extreme dilution or under constant volume, the molecular attractions play no part, this point is the most important with regard to liquids, when heating causes a change of volume. We shall trace this out numerically, and first remark that, in accordance with expectation, the specific heat of gases at constant volume is not altered by strong compression; Mallard and Le Chatelier went to the extent of 7,000 atmospheres, so that it is reasonable to suppose that in liquids too the specific heat at constant volume has the same value as in the vapour, to which is to be added the work of expansion when a change in volume occurs; and in liquids, in which a dissociation of double molecules occurs, that also must be taken into account.

As the simplest case, we will take liquid mercury, which very possibly consists of monatomic molecules in the liquid form also. According to p. 62, the specific heat of the

vapour at constant volume may be calculated from the kinetic theory as 3 per kilogram-molecule, i.e. $\frac{3}{200} = 0.015$ per kilogram. In liquid mercury the work of expansion must be added to this.

To calculate this we will assume that the internal molecular attraction is a force proportional to the square of the density, and so inversely as the square of the volume of a kilogram—the so-called specific volume—or

$$K = \frac{a}{V^2}.$$

Then the work of expansion is

$$A = \int \frac{a}{V^2} dV = -\frac{a}{V} + \text{const.},$$

or in expanding from V_1 to V_2

$$A = a\left(\frac{1}{V_1} - \frac{1}{V_2}\right),$$

in which a may be calculated from the internal latent heat of evaporation L. The latter represents the work done in expanding to the very great volume of the vapour [1]. So we get

$$L = a\left(\frac{1}{V_l} - \frac{1}{V_d}\right) = a(D_l - D_d),$$

in which V_l V_d are the volume of the liquid and vapour respectively, D_l and D_d their densities, so that mostly the second term is negligible, and we have simply

$$L = aD_l,$$

in which for mercury at 350°

$$L = 56.$$

The work of expansion per degree at that temperature, since the coefficient of expansion is then 0.00026, is

$$A = a\left(D_l - \frac{D_l}{1.00026}\right) = 0.00026 aD_l = 0.00026 \times 56 = 0.015,$$

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[1] Bakker, 'Inaugural dissertation,' 1888.

hich with the 0·015 given above for the increase in kinetic
iergy of molecular movement makes 0·03, a number in
ir agreement with the actual specific heat 0·032 of
ercury at that temperature [1].

Whilst, therefore, in the case of mercury, which consists
: free atoms, the specific heat may be calculated imme-
ately from the latent heat of evaporation, in the case of
odies with polyatomic molecules the specific heat in the
rm of gas or vapour at constant volume is needed—
quantity that cannot be calculated, but can be obtained
· experiment. Thus, e.g. for ethyl ether between $25°$
id $111°$ this is 0·4, and as the heat of evaporation is 90
id the coefficient of expansion 0·0017, we get for the
ecific heat of liquid ether

$$0·4 + 90 \times 0·0017 = 0·553,$$

hich again agrees approximately with the facts.

Difference between Specific Heat of Liquid and Vapour.

If we combine the relation of p. 64

$$L = a D_t,$$

hich holds for temperatures well under the critical point,
ith the law of rectilinear diameter, according to which at
ch temperatures the density of the liquid falls off linearly
ith the temperature, it follows that the latent heat of
aporation must do so too. It follows, however, from
outon's rule that this diminution must be the same for
olecular quantities of different substances, since at the
solute zero and at any other corresponding temperatures
e molecular latent heat is proportional to the critical
mperature. We have thus for any pair of bodies

$$L_{a T_k} : L'_{a T'_k} = T_k : T'_k = L_0 : L'_0,$$
$$L_{a T_k} - L_0 : L'_{a T'_k} - L'_0 = T_k : T'_k;$$

that $\dfrac{L_{a T_k} - L_0}{a T_k}$ or $\dfrac{\Delta L}{\Delta T} = \text{const.}$

In the above calculation it is assumed as a first approximation that a
ndependent of the temperature: the actual values for the two parts of
· specific heat probably differ a good deal from those calculated.

On the other hand, the change in the latent heat of evaporation is equal to the differences between the specific heats of the liquid and vapour, so that we find a constant value for the latter quantity also.

The variation from this rule which must obviously occur when in the liquid, rise of temperature results in decomposition of double molecules, will diminish the fall in the latent heat, or even convert it into a rise ; thus ethyl alcohol shows a minimum in the neighbourhood of 10° : the latent heat of evaporation is 220·9 at 0°, 211·2 at 10°, 220·6 at 20°.

4. *Specific Heat of Solids.*

Although the solid state lies almost outside the region of theoretical treatment, the specific heat of solids must be discussed, because the numerical values of it are connected with atomic weights by Dulong and Petit's law. We shall, therefore, in this instance put the empirical material in the foreground, and only in concluding touch on its relation to theory.

(a) *The Law of Dulong and Petit.*

It is well known that Dulong and Petit found that the specific heats of the elements in the solid state are, on the whole, about proportional to their atomic weights, and that the product of specific heat into atomic weight—the so-called atomic heat—is about 6.   In physical language it may be said that to raise the atomic quantity in kilograms from 0° to 1° requires about six calories.   Thus, e. g. copper with atomic weight 63 has a specific heat of 0·095.

This relation hardly possesses the character of a general rule, but the exceptions are associated with other properties, and are only very marked for elements with small atomic weights; from potassium (39) onwards the greatest deviation of the atomic heat—always greater than 6—is for iodine 6·9.   For smaller atomic weights the larger deviations occur, in the form of abnormally small specific

heats, especially for elements with small atomic volumes, as appears from the following table :

Element	Sp. heat	At. wt.	At. heat.	At. volume
Lithium . .	0.9408	7.03	6.6	11.9
Beryllium .	0.4084	9.1	3.79	4.3
Boron . . .	0.254	11	2.79	4.1
Carbon . .	0.1469 (Diamond)	12	1.76	3.4
Sodium . .	0.2934	23.05	6.76	23.7
Magnesium .	0.2499	24.36	6.09	13.3
Aluminium .	0.2143	27.1	5.8	10.1
Silicon . .	0.163	28.4	4.63	11.4
Phosphorus .	0.202	31	6.26	17
Sulphur . .	0.1776	32.06	5.7	15.7
Potassium .	0.1655	39.15	6.47	45.5

To a certain extent then the atomic heat is a periodic function of the atomic weight, like the atomic volume. Only the deviations in the first period, lithium to sodium, are very large, with 1.76 as minimum for carbon ; in the second period, sodium to potassium, much smaller, with 4.63 as minimum for silicon, whilst after potassium the values no longer falling below 6, but still with minima for the small atomic weights.

It has often been attempted, but with little success, to refer the variations from Dulong and Petit's law to secondary causes. Spring pointed out the possibility that the work of expansion might affect the values differently, and measured the specific heat of some alloys (d'Arcet's and others) which show a minimum of density, in the neighbourhood of the minimum, but without arriving at any clearly marked regularities [1]. Weber found that the abnormally low atomic heats of carbon, boron, and silicon approach 6 on rise of temperature. Thus the atomic heats are :

Graphite at 1000°		5.58
Boron	233°	4.03
Silicon	232°	5.7

This is in accordance with the observation that small atomic heats are associated with small atomic volumes.

[1] See also Richarz, *Wied. Ann.* 48. 712.

Also Behn[1] found that the atomic heats of other elements fall much below 6 at low temperatures, changing from 6.3 to 4 in the case of iron if the range of temperature, instead of 18° to 100°, be taken as $-79°$ to $-186°$.

(β) *Application of Specific Heat to determine Atomic Weight.*

Since for atomic weights above 39 the atomic heat is, not exactly it is true, but approximately 6.5, it is possible to determine atomic weights from the relation

$$A = \pm \frac{6.5}{S},$$

which indeed does not give an exact value, but may serve to decide if the choice lies between two considerably diverse values; that is frequently the case in atomic weight determinations, and may be illustrated by an historical example. When Mendelejeff proposed the periodic system, indium presented a difficulty: the atomic weight 76 was attributed to it, and such a value would not suit the system, coming between the elements arsenic and selenium,

$$\text{As } 75, \qquad \text{Se } 79.$$

But Mendelejeff remarked that the analysis of the chlorides,

$$38 \text{ indium to } 35.4 \text{ chlorine,}$$

may be interpreted by means of other atomic weights for indium, since 76 is based on the assumed formula

$$\text{In}Cl_2,$$

whilst e.g. $\text{In}Cl_3$ leads to the value

$$76 \times \tfrac{3}{2} = 114,$$

which just fills up a gap in the periodic system between cadmium and tin

$$\text{Cd } 112, \qquad \text{Sn } 119.$$

In such a case the specific heat is an assistance; it was

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[1] *Wied. Ann.* 1898, p. 242.

determined by Bunsen to be 0·057, and the choice is then no longer doubtful, since

$$0 \cdot 057 \times 76 \quad = 4 \cdot 3,$$
$$0 \cdot 057 \times 114 = 6 \cdot 5,$$

so that only the atomic weight 114 agrees with Dulong and Petit's law.

(γ) *Additive Character of the Specific Heat of Solid Bodies* (*Neumann's Law*).

Whilst Dulong and Petit determined the relation between the elements with regard to their specific heat, Neumann did the same for the relation between a compound and its components, and arrived at a simple additive rule, that the heat necessary for the molecular quantity of a compound (M_w) is the sum of the atomic heats (A_w) of the components; a compound therefore behaves in this respect, as in respect to its weight, as a mixture, although only approximately. Symbolically this may be expressed as

$$M_w = \Sigma A_w,$$

or since the atomic heats are approximately 6·5,

$$M_w = 6 \cdot 5 \times n,$$

where n is the number of atoms of which the molecule is composed. It must be remembered that the last expression only holds for compounds of such elements as follow Dulong and Petit's law.

As example we may take iodide of lead PbI_2, whose elements, being of high atomic weight, fall under Dulong and Petit's rule. Then we should have

$$M_w = 3 \times 6 \cdot 5 = 19 \cdot 5,$$

and the specific heat (S_w) of lead iodide, with molecular weight $207 + 2 \times 127 = 461$,

$$S_w = \frac{19 \cdot 5}{461} = 0 \cdot 042.$$

An application of Neumann's rule is to determine approxi-

mately the specific heat of elements which cannot be directly measured in the solid state. Oxygen may be taken as example, and its specific heat determined from that (0·156) of Fe_3O_4. We have then

$$M_w = 232 \times 0.156 = 36.2$$

$$M_w = \Sigma A_w = 3 \times 6.5 + 4x = 36.2 \qquad x = 4.17,$$

so that the atomic heat of oxygen should be 4·17.

(δ) *Theoretical Indications.*

Whilst experimental research has not succeeded in putting Dulong and Petit's law into stricter form, and on the other hand the solid state has not yet been satisfactorily brought within the region of molecular-mechanical concepts, one is driven on the theoretical side to possibly accidental relations towards explained facts.

In the first place, it must be observed that the phenomena are simpler in the case of solids than liquids because the work of expansion hardly comes into consideration, and the specific heats at constant volume hardly differ from the values forming the basis of Dulong and Petit's law. In the second place, the complication due to formation and decomposition of double molecules occurring in liquids is possibly absent in solids.

It is then striking how the atomic heats of solids are quantitatively associated with that for gaseous mercury, which is found both by theory and experiment to be 3. It is noticeable that the probably monatomic metallic elements have in no case so far given an atomic heat lower than this, and it appears from Behn's experiments that 3 is the lower limit for some of them.

Element	Atomic heat		
	100° *to* 18°	18° *to* − 79°	− 79° *to* − 186°
Copper . . .	6	5·6	4·5
Nickel . . .	6·4	5·8	4·3
Iron . . .	6·3	5·6	4
Aluminium .	6	5·3	4·2

The values lying below 3 are for elements such as

carbon, whose molecules very probably consist of several atoms.

On the other hand, the highest values so far found are about twice three, and only exceed that amount by a little, while if the work of expansion were taken into account they would be smaller still.

With these considerations may be taken Richarz's assumption that in solids the atoms move about centres, and that rise of temperature consists partly in an increase of the kinetic energy of this motion, requiring, as in gases, three calories per kilogram atom. To this is to be added the increase of potential energy, which if the rotation about a fixed point followed the Newtonian law of attraction, would be equal to the increase in kinetic energy, making in all six calories, in accordance with Dulong and Petit's result.

§ 5. CAPILLARITY AND SURFACE TENSION.

A. Observations.

The molecular attractions which are apparent even in gases, and there produce a deviation from Boyle's law in the sense of a reduction of the pressure caused by molecular collisions (i. e. a retardation of the movement outwards) in liquids, stop this movement outwards altogether. Whilst gases tend to increase their volume, in liquids an opposite tendency occurs, or an internal pressure. This is the cause of the relatively great density of liquids, and of their assumption of the smallest possible surface, which in the absence of external forces is spherical. In many respects, therefore, a liquid is comparable to a gas enclosed in an elastic membrane, such as a soap bubble, only that the elasticity, here depending on the membrane, is in the liquid caused by internal attractions. The tension thus existing in the surface layer of a liquid is called surface tension, and shows itself in the first place as a force tending to reduce the surface of the liquid. Any force, then, that

tends to increase the area of the liquid surface meets a resistance, and the shape of the liquid changes, with increase in surface, until equilibrium is reached.

In the numerous methods for measuring the surface tension the force employed to increase the surface is mostly the weight, and most simply by the use of a capillary tube. We shall restrict ourselves to this method because, in the form worked out by Ramsay and Shields, it is so far the most important for the relations between surface tension and other properties.

We may next roughly describe the simpler apparatus used for the purpose.

It consisted [1] of a capillary tube which could be raised or lowered at will, so that the meniscus of liquid sucked up into it, when observed, was always at the same level, thus making the results more comparable. The capillary and the liquid were contained in a tube that could be evacuated, and sealed up, and surrounded by a vapour jacket, so as to maintain a suitable constant temperature. The arrangement for raising and lowering was an electromagnet outside the whole apparatus, acting on a piece of iron attached to the capillary.

B. Molecular Weight and Surface Tension.

It is of importance to test the reliability of the assumptions on which depend the various proposals for determining molecular weights of liquids. It has already been pointed out that the methods discussed in this Third Part are inferior to those dealt with in Part II, depending on Avogadro's law, and the corresponding laws of dilute solutions, since it is only the latter that rest on a satisfactory theoretical basis. A similar research, not, however, yet accomplished, lies in the characteristic equations of liquids, which all need, in order to harmonize with the facts, a purely

empirical modification, and consequently offer no certain basis for molecular weight determinations.

The phenomena, even at the critical point, are uncertain, since they require the empirical rule of Young, given on p. 23. Below the critical temperature the law of correspondence gives a point of departure, since formation of double molecules in the liquid, as explained on p. 26, causes a fall in the concentration of simple molecules in the vapour ; this may be concluded on kinetic grounds of a trustworthy nature, so that if the vapour, as evidenced by its density, consists only of simple molecules, a fall in its concentration and deviation from the law of the rectilinear diameter must occur in corresponding measure. Hence it is concluded that molecular association in liquids is indicated by abnormally large volume of the saturated vapour (p. 26), abnormally small vapour pressures (p. 47), together with deviation from the formula given on p. 47, abnormally high boiling point of the liquid (p. 53), and abnormally high heat of evaporation (p. 58) ; these four indications are necessarily associated together, and must be distinguishable in the specific heat as well.

The methods for determining molecular weight which do not belong to this group, such as that of Guye by the critical coefficient, and that of Traube from the density, are still less reliable *a priori*, although it must not be concluded that they lead to false results. Granting this, we may next discuss how far the conclusions of Eötvös, Ramsay, and Shields on molecular weight of liquids from capillary phenomena are justified.

Surface tension. Starting from the capillary rise, it must first be noticed that this depends on the bore of the tube, so that the latter factor must be eliminated. The height is independent of the nature of the capillary wall, whether glass or not, if only the liquid wets it, so that the capillary attraction proceeds from the film of liquid adhering. The capillary being previously moistened, we have practically a liquid skin, and when the meniscus rises h cm. the area,

of the surface is diminished by $2\pi rh$ (r is the radius in centimetres); if γ is the work done on diminishing the area by one square cm., the so-called surface energy, the total work done is

$$2\pi rh\gamma \text{ in gram-centimetres.}$$

This work is spent in raising a column of liquid of weight $\pi r^2 h D$ (where D is the density referred to water) through a height h cm. requiring an amount of work

$$\pi r^2 h^2 D$$

so that

$$2\pi rh\gamma = \pi r^2 h^2 D,$$

whence

$$\gamma = \tfrac{1}{2} rh D \text{ in gram-centimetres.}$$

Taking into account the pressure of vapour the work gained by the diminution in surface consists of two parts, due to the change in surface of the liquid and vapour, and obviously of opposite signs, so that the total amount is

$$2\pi rh\,(\gamma_l - \gamma_r),$$

in which, at the critical point,

$$\gamma_l = \gamma_r;$$

we may, however, retain the simple value γ provided we understand by it the total work gained in the reduction of surface of both the liquid and vapour.

In the same way the total work done in raising the level of the liquid in the capillary is modified, and if the densities of the liquid and vapour referred to water are D_l and D_r, to

$$\pi r^2 h^2 (D_l - D_r), \text{ whence } \gamma = \tfrac{1}{2} rh\,(D_l - D_r).$$

Influence of temperature. The capillary rise obviously becomes zero at the critical temperature, on account of the identity between liquid and vapour; so that it must eventually fall with increase of temperature. The fall is found to be approximately proportional to the rise of temperature, as appears from the following table for ether :

Temp. t	Rise h	$-10\dfrac{\Delta h}{\Delta t}$	Temp. t	Rise h	$-10\dfrac{\Delta h}{\Delta t}$
20°	3·74 cm.		140°	1·215 cm.	0·195
		0·23	150°	1·000 ,,	0·215
50°	3·04 ,,	0·21	160°	0·785 ,,	0·215
60°	2·83 ,,	0·19	170°	0·57 ,,	0·215
70°	2·64 ,,	0·21	180°	0·35 ,,	0·22
80°	2·43 ,,	0·165	185°	0·23 ,,	0·21
90°	2·265 ,,	0·215	188°	0·16 ,,	0·23
100°	2·05 ,,	0·22	191°	0·075 ,,	0·28
110°	1·83 ,,	0·21	193°	0·031 ,,	0·22
120°	1·62 ,,	0·21	194·5°(crit.)	0 ,,	0·21
130°	1·41 ,,				

The constant change in the capillary rise due to temperature, is, of course, different for a different radius of the capillary tube, but being, according to p. 74, inversely proportional to the latter, the change

$$\frac{\Delta h\, r}{\Delta t}$$

is independent of the tube and characteristic for each liquid.

Relation to molecular weight. A striking relation between surface energy and molecular weight was discovered by Eotvös, Ramsay, and Shields, and shows itself in the approximate constancy of the change in the molecular surface energy with temperature. The molecular surface energy is here defined as the work necessary to enlarge the surface by an amount on which a mass proportional to the molecular weight lies, the molecules being treated as spheres. The quantity in question is therefore

$$\gamma M_v^{\frac{2}{3}},$$

where M_v is the molecular volume, i.e. the molecular weight in grams divided by the density.

We will first trace the constancy of the change in this function with temperature, in the case of a definite substance, ether, the surface energy being in ergs instead of gram-centimetres, by multiplication by 981.

Temp. t	$\gamma M_v^{\frac{2}{3}}$	$-\dfrac{\Delta\gamma\, M_v^{\frac{2}{3}}}{\Delta t}$	Temp. t	$\gamma M_v^{\frac{2}{3}}$	$-\dfrac{\Delta\gamma\, M_v^{\frac{2}{3}}}{\Delta t}$
20°	363.7		120°	143.6	
		2.315			2.16
40°	317.4		130°	122	
		2.14			2.16
50°	296		140°	100.4	
		2.32			2.17
60°	272.8		150°	78.7	
		2.18			2.01
70°	251		160°	58.6	
		2.15			1.96
80°	229.5		170°	39	
		2.14			1.91
90°	208.1		180°	19.9	
		2.12			1.52
100°	186.9		185°	12.3	
		2.16			1.34
110°	165.3		190°	5.5	
		2.17			1.22
120°	143.6		194.5°	0	

It seems then that this quantity is constant up to temperatures about 50° below the critical point.

In a comparison between 36 substances the change of molecular surface energy was found to vary between 2·31 and 1·92, as shown by the following table:

Substance	$-\dfrac{\Delta\gamma\, M_v^{\frac{2}{3}}}{\Delta t}$	Substance	$-\dfrac{\Delta\gamma\, M_v^{\frac{2}{3}}}{\Delta t}$
$Ni(CO)_4$	2·31	C_8H_{18}	2·22
C_2H_5SCN . . .	1·92	CCl_4	2·1
CS_2	2·02	C_2H_5I	2·1
N_2O_4	2·11	$HCOOCH_3$ . . .	2·04
$SiCl_4$	2·03	Quinoline	2·43
PCl_2.	2·1	Paraldehyde . . .	2·37
S_2Cl_2	2 2		

It is striking to note how hydroxylic liquids that, on other grounds are thought to be associated, here too are abnormal.

Methyl alcohol	0·93
Formic acid	0·9
Water	0·87

C. Theoretical Relations.

On account of the ease and accessibility of Ramsay and Shields' method, it is of importance to discuss its theoretical basis, to see how far the conclusions must be regarded as binding.

For this reason we may consider what relations exist between the Eotvös-Ramsay rule, and that of Mathias on the rectilinear diameter.

According to p. 28 the expression for Mathias' rule is

$$D_l + D_r = a - bT,$$

where D_l and D_r are the densities of the liquid and vapour respectively. If the latter is negligible by comparison with the former, as is the case at some distance from the critical temperatures, at which also the Eotvös-Ramsay rule first becomes applicable, then

$$D_l = a - bT.$$

From this it appears, according to p. 65, in conjunction with the rule of Deprez-Trouton for corresponding states, that we get the simple result

$$\frac{\Delta L}{\Delta T} = \text{const.},$$

i. e. the diminution of the latent heat with temperature, when not too near the critical point, has a constant value for those substances in which a formation and decomposition of double molecules do not occur.

But the latent heat of evaporation is associated with the surface energy[1], since if we neglect the influence of the vapour, a molecule, in passing from the interior of the liquid to the surface escapes from one-half of the internal attraction, while on evaporation it escapes altogether. If L is the internal latent heat of evaporation, for which the law of Deprez and Trouton holds,

$$\gamma M_v^{\frac{2}{3}} = \tfrac{1}{2} L,$$

so that

$$\frac{\Delta \gamma M_v^{\frac{2}{3}}}{\Delta T} = \text{const.}$$

in accordance with the law of Eotvös and Ramsay.

§ 6. Optical Relations.

We have restricted ourselves, in dealing with the relations between physical properties and constitution, to what can be approximately brought under a single point of view

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[1] Stefan, *Wied. Ann.* 29. 655.

by means of the characteristic equations, and such more or less rationally based empirical relations as are associated with these. The phenomena of the refraction of light belong to this class, because, on the one hand additive relations are found on comparing different substances, closely resembling those discovered in regard to volume, and on the other, this parallelism, together with the dielectric constant, affords a certain theoretical basis.

A. Velocity of Light and Refractive Index.

The velocity of light has its highest value *in vacuo*, so that the decrease in other media may be associated with the greater or smaller space occupied by matter, the measure of which we have so far taken to be the volume at the absolute zero, so that to measure the velocity of light at that temperature would be a matter of much importance.

The ratio of the velocities in two media is known to be given by the refractive indices, since, according to Snellius :

$$\frac{v_1}{v_2} = \frac{\sin L}{\sin r} = n;$$

where L is the angle of incidence (angle with the normal to the surface in the medium to which the index 1 refers), r the angle of refraction, n the refractive index calculable from the two numbers, and which accordingly as v_1 refers to vacuum, is always greater than unity. The refractive index is, however, often given relatively to air, thus causing a reduction in the numerical value of constant relative amount, but small, since the refractive index of air is only slightly greater than unity.

B. Influence of Wave-length.

Whilst to start with we compare optical relations between different substances to the corresponding volume relations, we must now remark on a fundamental fact which makes the problem much more complex. Whilst in the volume

we have a definite quantity to deal with, which only depends on the state of the body, here the nature of the light plays a part also, since the velocity of light depends on its colour, i. e. on its wave-length. It is only in a vacuum that there is no difference in this respect; the partial occupation of space by matter causes a fall in velocity which is different for different colours. This varying influence causes the phenomenon of dispersion, i. e. the separation of light of different colours, or formation of a spectrum, and the first question is to express the effect exerted on different kinds of light in an intelligible manner, by representing the refractive index as a function of the wave-length (λ). This has not yet been accomplished, since the formula of Cauchy :

$$n = A + \frac{B}{\lambda} + \frac{C}{\lambda^2},$$

serves only for bodies of normal dispersion, whilst the newer formulae which take abnormal dispersion into account, do not fit the observations with the certainty desirable. We are therefore driven to avoid this difficulty by dealing only with the relations discoverable by using light of a single wave-length [1]. Measurements refer mostly to sodium light n_D.

C. Effect of Density.

Not only the wave-length of light, but also the condition of the body in question influences the refractive index. It has been found that the influencing cause is the density of the substance rather than its temperature or state of aggregation, which is in accordance with the fundamental point mentioned on p. 78, that it is the occupation of space by matter that affects the velocity by light. The influence can be traced numerically by the method of Lorenz and Lorentz, the former [2] starting with the as-

[1] Graham-Otto Landolt, 1898, i, iii. 2. 576.

[2] *Wied. Ann.* 11. 70.

sumption of spherical molecules in the interstices of which light moves with the same velocity as *in vacuo*. The relation between the density D and the refractive index n referred to vacuum, then becomes

$$\frac{n^2 - 1}{(n^2 + 2)\,D} = k.$$

This formula, though not in all respects satisfactory, expresses satisfactorily the observations on the influence of temperature and states of aggregation, with which it is in the first instance concerned, as is shown by the following observations of Eykmann [1] taken at widely different temperatures :

Substance		Temperature	$\dfrac{n_\alpha^2 - 1}{(n_\alpha^2 + 2)D}$
Isosafrol	$C_{10}H_{10}O_2$	$17 \cdot 6°$	0 2925
		$141 \cdot 1°$	0·2962
Diphenylethylene .	$C_{14}H_{12}$	$22°$	0·3339
		$143 \cdot 4°$	0·3382
Quinoline	C_9H_7N	$16 \cdot 2°$	0·3187
		$141°$	0·3225

For change of state, Lorenz, e. g. found the following numbers :

Substance	$\dfrac{n^2_D - 1}{(n^2_D + 2)D}$	
	Liquid at $10°$	*Vapour at* $100°$
Water	0·2068	0·2061
Carbon disulphide	0·2898	0·2805
Methyl iodide	0·1571	0·1557
Ethyl ether	0·3068	0·3026

D. Additive Relations.

The close relation of the refractive index to the occupation of space by matter harmonizes with the additive relations found to hold for both quantities, only that the volume to be considered is essentially that at the absolute zero, or the values in the critical or other corresponding states, which are proportional to the former ; whereas

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[1] *Rec. des trav. Chim. des Pays-Bas*, **12.** 163 ; **14.** 185. n_α refers to the red hydrogen line.

with regard to refraction the above constant k is to be taken.

The chief result is that the so-called molecular refraction :

$$Mk = M \frac{n^2 - 1}{(n^2 + 2) D},$$

may be calculated by summation from the values for the components.

We will again adopt the most radical method, obtaining first the numbers for the elements : the indices refer to the sodium line [1], A_g is the atomic weight, A the atomic refraction :

Element	n	$A_g \dfrac{n^2 - 1}{(n^2 + 2) D} = A$
Bromine	1.001132	8.46
Chlorine	1.000773	5.78
Oxygen	1.000272	2.03
Nitrogen	1.000296	2.20
Hydrogen	1.000143	1.07
Carbon (diamond)	2.46986	2.15

The following are some binary compounds :

Compound	n	$M \dfrac{n^2 - 1}{(n^2 + 2) D}$	ΣA
Hydrobromic acid . .	1.000573	8.57	9.53
Hydrochloric acid . .	1.000447	6.68	6.85
Water	1.000259	3.86	4.17
Nitrous oxide . . .	1.000516	7.69	6.43
Nitric oxide	1.000297	4.43	4.23
Ammonia	1.000379	5.65	5.41
Methane	1.000444	6.71	6.43

Additive relations unmistakably exist, but exactness fails, as almost ever. The deviations, as in the case of the molecular volume are referred to constitutive influences, to determine which organic compounds offer a rich field. It must be borne in mind that owing to varying dispersion, and the failure of attempts to reduce refractive indices for different colours to a common standard, strict additivity is not to be expected; rather if it existed for any one

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[1] Brühl, *Zeitschr. f. Phys. Chem.* 7. 1.

colour, it would necessarily partly fail for other wave-lengths.

Accordingly the approximate equality of refraction shown by organic isomers is very striking, more so than in the case of volumes, e. g.

Substance	$M\dfrac{n_a^2-1}{(n_a^2+2)\,D}$
{ Valerianic acid	26.72
{ Methyl butyrate	26.79
{ Ethylene chloride	20.96
{ Ethylidene chloride	21.08
{ Athyl alcohol	16.85
{ Propyl aldehyde	15.93
⌠ o-Cresol	32 52
⎬ m-Cresol	32.56
⌡ p-Cresol	32.57
{ Fumaric acid	70.89
{ Maleic acid	70 29

Since then equal differences in composition are associated with equal differences in molecular refraction, the atomic refractions may be determined indirectly and were found by Landolt for n_a to be

$$H = 1.04, \qquad O = 2, \qquad C = 2.48.$$

But then, just as in the relations of volume, the mode of combination appears to have an essential influence, so that e.g. for aldehyde

$$H_3CC\!\!\diagup^{\displaystyle O}_{\displaystyle H}$$
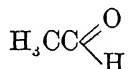
$M_a = 11.5$, and deducting $2 \times 2.48 + 4 \times 1.04$, there remains for oxygen 2.38, on the other hand for acetic acid

$$H_3CC\!\!\diagup^{\displaystyle O}_{\displaystyle OH}$$
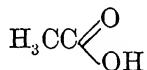
$M_a = 12.93$, and deducting 11.5, there remains for oxygen 1.43.

Double-linked oxygen regularly shows a higher atomic refraction, and the same is true for double-linked carbon as compared with single-linked.

But even for univalent elements, such as the halogens, where there is no possibility of different linkages, small but regular differences are observed, thus :

		A				
Chlorine	5.62	to	6.37	mean	6.014
Bromine	8.64	,,	9.06	,,	8.863
Iodine	13.58	,,	13.91	,,	13.808

again in fair agreement with the values given on p. 81, for the free elements. The additive character is thus far-reaching in the region of optics. Finally we should have to discuss the connexion with the relations of volume were it not that heat of formation causes the essential moment to lie in constitutive influences.

E. Dielectric Constant.

Just as light travels fastest in a vacuum, so the attracting and repelling action of electric charges is greatest (a) if vacuum separates them, whilst in a space partly filled with matter the forces are diminished to a fraction, say $\dfrac{a}{K}$. The quantity K in this expression is the so-called dielectric constant, and the diminution of electric action may be explained by assuming that matter is conducting for electricity, vacuum not. This connexion between electricity and light, which finds its mathematical expression in the electromagnetic theory of light, leads by the help of that theory to a simple relation between the dielectric constant and the refractive index for infinitely long wave-length (N) viz. :

$$K = N^2.$$

The latter may be calculated for substances of normal dispersion from Cauchy's formula [1], and the relation thus brought out numerically. The numbers are for 18° and atmospheric pressure :

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[1] Landolt and Jahn, *Zeitschr. f. Phys. Chem.* 10. 300.

Substance	Refractive index	Dielectric constant		
Hydrogen	1·00014	1·000264	=	1·00013^2
Carbon dioxide . .	1·00045	1·00097	=	1·00048^2
Hexane	1·3683	1·8536	=	1·3608^2
Octane	1·3902	1·9382	=	1·3899^2
Decane	1·4001	1·9641	=	1·4015^2
Benzene	1·4816	2·2221	=	1·4777^2

Since the calculation involves an uncertain extrapolation to infinite wave-length by Cauchy's formula, which is not applicable to the purpose in the case of bodies with anomalous dispersion, the direct measurement of refractive index for Hertzian waves[1] of very long wave-length (6 m.) affords a very useful completion; the highest refractive indices so observed were

$$\text{castor oil} \quad N = 2·05 \qquad K = 4·67 = 2·16^2.$$
$$\text{water}[2] \quad N = 8·91 \ (17°) \quad K = 80 = (8·99)^2.$$

On the other hand Clausius and Mossotti found a relation between dielectric constant and space occupied, on the assumption of spherical molecules:

$$K = \frac{1 + 2d}{1 - d},$$

in which d is the fraction of the total volume actually occupied by matter. The expression represents the diminution of dielectric constant down to unity for indefinite dilution, and on the other hand its increase with increasing density by condensation or cooling[3], as for benzine, e. g.

Liquid at 19·6, $K = 2·218$. Vapour at 100°, $K = 1·0027$.

Since d is proportional to the density D we have for a given body:

$$\frac{K - 1}{D \, (K + 2)} = \text{const.,}$$

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[1] Arons and Rubens, *Wied. Ann.* 42. 581 ; 44. 206.

[2] Cohn, Zeeman, *Wied. Ann.* 57. 15 (1896).

[3] Abegg and Seitz, *Zeitschr. f. Phys. Chem.* 29. 242.

a result that is approximately confirmed by the values for benzene, since

$$D_{19 \cdot 6} = 0 \cdot 88 \qquad D \text{ at } 100° \text{ and } 760 \text{ mm.} = 0 \cdot 0026,$$

whence

$$\frac{K_1 - 1}{D_1(K_1 + 2)} = \frac{1 \cdot 218}{0 \cdot 88 \times 3 \cdot 218} = 0 \cdot 43 ;$$

and

$$\frac{K_2 - 1}{D_2(K_2 + 2)} = \frac{0 \cdot 0027}{0 \cdot 0026 \times 3 \cdot 0027} = 0 \cdot 34.$$

There is therefore no exact agreement, but a somewhat extensive approximation[1], and we shall consequently mention a further relation, pointed out by Guye.

Since

$$d = \frac{K - 1}{K + 2} \quad \text{and} \quad K = N^2,$$

it follows that

$$d = \frac{N^2 - 1}{N^2 + 2},$$

and the volume M_v actually occupied by the molecular weight M

$$M_v = \frac{M}{D}\, d = \frac{N^2 - 1}{(N^2 + 2)\, D}\ M = MR,$$

the molecular refraction for infinite wave-length. This serves to explain the additive properties of the molecular refraction, the quantity in question being a measure of the space occupied by matter, and since the critical coefficient $\frac{T_k}{P_k}$ according to p. 48 is so too, we have

$$\frac{P_k MR}{T_k} = \text{constant},$$

this is roughly the case[2]:

[1] Lebedew, *Wied. Ann.* 44. 304 ; Ratz, *Zeitschr. f. Phys. Chem.* 19. 94.

[2] Altschul, *Zeitschr. f. Phys. Chem.* 11. 595 ; Nasini, l. c., 16. 249.

	MR	$\dfrac{T_k}{P_k}$	Quotient [1]
Hexane	28·62	16·92	1·69
Octane	38·19	22·58	1·69
Decane	47·46	28·32	1·68
Benzene	25·16	11·25	2·24
Toluene	33·2	14·28	2·32
Ethylbenzene	38·86	16·24	2·39
o-Xylene	41·52	17·09	2·43
p-Xylene	35·65	17·66	2·02
m-Xylene.	37·82	17·3	2·19

Here the molecular refraction is calculated from the dielectric constant. An indication as to molecular weight is consequently given and the quotient accordingly falls to about 1·1 for the probably associated liquids, water, methyl, alcohol, and acetic acid.

[1] This quotient is much more constant when calculated from A in Cauchy's formula (Guye, *Bull. de la Soc. Chim.* (3) 13. 34).

II. RELATIONS BETWEEN CHEMICAL
PROPERTIES AND COMPOSITION

As in dealing with physical properties in regard to composition, so here there is a preliminary question to be answered, how the property in question is to be represented numerically in a manner as independent of other circumstances as possible. How far this can be answered in the case of the physical properties has appeared in the foregoing; the conditions are less favourable here, on account of the more complex character of chemical properties. Thus the way in which temperature affects volume is in many cases, such as the gases, known: the way in which it affects velocity of reaction has not yet been brought satisfactorily under a general view. Accordingly the relations with which we shall have to do now are throughout of an empirical character, and often merely qualitative. The arrangement must be made with a view to this, and refers to the chief rules which are of general application in this region of the phenomena considered [1].

[1] Note here a very important remark of Le Chatelier, 'Recherches expérimentales et théoriques sur les équilibres chimiques,' *Annales des Mines*, 1888, p. 193. According to this the dissociation pressure and other data referring to chemical equilibrium are associated with the Deprez-Trouton law. Thus for calcium carbonate $\frac{q}{T} = 23.4$ at the temperature for which the dissociation pressure is one atmosphere (q is the molecular heat of formation of $CaCO_3$ from lime and carbon dioxide). Unfortunately there are not at present data enough for an extended application, such as might be sought in the first place amongst salt hydrates.

§ 1. The elements bring the chemical properties that they show in simple binary compounds into more complex derivatives.   This appears most clearly with regard to valency, which for carbon in binary compounds such as CH_4 is four; Kekulé then proved that this fundamental property exists also in more complex compounds, and so laid the foundation for the study of chemical constitution.

§ 2. The elements exercise in their compounds other influences, which fall off with distance, and modify the original character of the element influenced in a way that can be brought under general rules.   A suitable example is the action of oxygen in organic compounds in decomposing and hastening reaction, and shows that changes almost always take place in its neighbourhood; so that, e. g. breaking up the carbon linkages by oxidation of ketones always takes place at the carbon atom which carries the oxygen atom.

§ 3. Sometimes grouping of elements leads to entirely new chemical properties which could not even be distantly expected from the rules contained in the two preceding paragraphs.   This peculiar behaviour is seen, e. g. in the sudden appearance of a strong basic character in ammonium derivatives such as $(H_3C)_4NOH$, which rivals caustic potash in properties.

§ 1. The Elements bring the Chemical Properties that they show in simple Binary Compounds into more Complex Derivatives.

To bring out this first relation as clearly as possible let us consider first the indications by which the chemical character is distinguished in simple binary compounds.

In the first place there is the valency: sometimes—in the elements that play the chief parts in organic chemistry, carbon, hydrogen, or oxygen—this is so constant, in the most diverse compounds, that it is a reliable guide to

determination of constitution in this department, and was discussed in that bearing in Part II.

In the next place must be considered the magnitude of the affinity which governs the sense of reaction and the phenomenon of chemical equilibrium : its measure is often simply found in the electromotive force, whilst the evolution of heat at the absolute zero depends on it, but suffers a modification with temperature that causes a displacement of equilibrium.

Characteristic, thirdly, is the velocity of reaction, but in accordance with the introduction of a new factor, time, it offers more difficulty towards simple treatment from the theoretical standpoint, so that here we are reduced to a considerable accumulation of empirical material.

We shall endeavour in the following to describe the chemical character of the best investigated elements in simple compounds according to the above principles, and then trace out how far it reappears in more complex derivatives.

A. Chemical Character of the most important Elements in their Simple Compounds.

1. *Positive or Metallic and Negative or Metalloid Character.*

It is well known that in judging the chemical behaviour of an element its so-called positive or negative character forms an important guide. Starting from Berzelius' electrochemical concepts as an essentially qualitative notion, it has begun in recent times to appear capable of quantitative treatment.

The theory of electrolytic dissociation affords the easiest insight into these phenomena, and the positive elements, such as potassium, are distinguished by it as possessing a strong tendency to the formation of positive ions, which is most marked in aqueous solution ; the negative or metalloid character, e. g. of chlorine, accordingly shows

itself in the opposite tendency to form negative ions. Here we stand on purely experimental ground if, e. g. the positive character is defined as leading to separation at the negative pole during electrolysis.

A direct measure of the facility of formation of positive ions or of the fixation of positive electricity is given in the electromotive force needed for the electrolysis of a binary compound, assuming that this electrolysis consists in a simple transformation of the ions into the ordinary state of matter, the compound consequently being present in solution only in the form of ions, as is the case with potassium chloride on sufficient dilution. The electrolysis then means that the chlorine and potassium ions, giving up their negative and positive electricity respectively, form chlorine and potassium, the first however in the state of diatomic molecules.

Hence it follows immediately that the electromotive forces applied to decompose binary compounds, as mentioned above, must be of an additive character, obtainable by addition of quantities referring to each ion, called by Nernst [1] 'Zersetzungsspannungen.' Assuming arbitrarily the value for hydrogen as zero, the values for normal solutions according to Neumann [2] are the following in volts : Affinity for positive electricity :

Na	Mg	Al	Mn	Zn	Cd	Fe	Tl	Ni	Co	Pb	Sn	Sb
+ 2.58	1.47	1.28	1.06	0.74	0.38	0.33	0.30	0.22	0.22	0.17	0.16	0.13

Bi	As	Cu	Ag	Hg	Pd	Pt	Au
− 0.25	0.31	0.34	0.78	0.79	0.82	0.94	1.10

Affinity for negative electricity :

$$Cl + 1.31, \qquad Br \ 0.94, \qquad I \ 0.52,$$

which is in accordance with the facts, for hydrochloric acid, e. g. in normal solution, is decomposed by an electromotive force of 1.31 volts, magnesium iodide by

$$1.47 + 0.52 = 1.99.$$

[1] *Berl. Ber.* 30. 1547.
[2] *Zeitschr. f. Phys. Chem.* 14. 193 ; 27. 57.

This electro-affinity determines, on the one hand, the direction in which a reaction will proceed in case one of the above elements comes into contact with a normal solution of one of the binary compounds, e. g. magnesium will displace zinc from its halogen compounds, and chlorine will displace bromine or iodine from combination with a metal. So too, the limit to which the displacement will take place may be worked out numerically from the above data.

Secondly, the data explains that binary compounds, of which one has a strong affinity for positive, the other for negative electricity, such as sodium chloride, have a tendency to break up into ions according to the equation :

$$NaCl + (+) + (-) = (\overset{+}{N}a) + (\overline{Cl}),$$
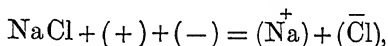
and that this is most to be expected when the attraction between positive and negative electricity is small, in media of high dielectric constant such as water.

Compounds of markedly negative elements such as chlorine would therefore lead to formation of positive hydrogen ions in such a medium, that is, show an acid character, and those of markedly positive elements such as sodium with hydroxyl to formation of negative hydroxyl ions, that is, show a basic character.

2. *Evolution of Heat in Simple Reactions.*

Effects of affinity may, as already explained, be followed quantitatively in association with the work which a reaction can perform. Since data are lacking we are driven to the accompanying evolution of heat, which, at the absolute zero would be equal to the work done, but at ordinary temperature will differ from that more or less.

A direct comparison may be made if from the heat of formation of binary electrolytes the heat of formation of the ions, or heat of ionization be calculated [1]. Again, taking

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[1] Ostwald, *Lehrbuch*, 1893, ii. 953.

that of hydrogen as zero, in ordinary calories per gram-ion the results are:

Na	Mg	Al	Mn	Zn	Cd	Fe″	Tl	Ni	Co
56.5	53.6	39.4	24.2	16.6	8.3	10.1	− 1	7	7.6

Pb	Sn″	Cu″	Ag	Hg′
− 0.7	0.7	− 8.9	− 26.4	− 20.7

for formation of positive ions: and for negative

$$\text{Cl } 39.9 \qquad \text{Br } 28.9 \qquad \text{I } 13.7,$$

from which it follows, e. g. that the formation of hydro-chloric acid in aqueous solution is accompanied by an evolution of 39.9 calories, sodium chloride by

$$39.9 + 56.5 = 96.4.$$

Since a volt per gram equivalent in the table p. 90 means 23.09 calories, we may compare the work and heat, and arrive for sodium at $2.58 \times 23.09 = 59.6$ as work against 56.5 as heat; for chlorine 30.2 against 39.9, and so on. But in comparing these values it must be borne in mind that at any temperature but the absolute zero, the work depends greatly on concentration, since the work done on dilution to n times normal solutions has to be subtracted, and amounts to $0.002 \times \log_e n$ calories per gram-ion, which for a decinormal solution is 1.4 cal.

Allowing for this, we may first note what is character-istic of the metallic nature in these thermochemical data. This is most marked for potassium, to which the following numbers refer, giving the heat of formation of the equivalent quantity, and subsequent solution in water:

½ S. aq.	½ O. aq.	F. aq.	Cl. aq.	Br. aq.	I. aq.
55.6	82.3	113.1	101.2	90.2	75

The relation expressed by the following formula is characteristic, and recurs among the typical metals:

$$(M . S_{\frac{1}{2}}) < (M . O_{\frac{1}{2}}) < (M . F) > (M . Cl) > (M . Br) > (M . I),$$

it holds even for metals of the smallest thermochemical values such as silver:

[1] S	$\frac{1}{2}$ O	F	Cl	Br	I
1.6	3.0	26.7	29.4	22.7	13.8

only that the heat of combination of fluorine is out of place, because it refers to the dissolved salt, for which the numbers for the chloride bromide and iodide would be 13.6, 2.4, and − 13.1.

It is quite otherwise with the elements that are commonly known as non-metals. We will arrange the data for these in a table alongside of those for sodium by way of comparison ; the numbers are again for formation of the product in aqueous solution, so far as that exists.

	Na	H	$P_{\frac{1}{3}}$	$C_{\frac{1}{4}}$	$S_{\frac{1}{2}}$	$N_{\frac{1}{3}}$	$O_{\frac{1}{2}}$	Cl
$S_{\frac{1}{2}}$	51	4	—	− 7	0	− 11	39	4
$O_{\frac{1}{2}}$	78	34	42	24	39	− 1	0	− 4
Cl	96	39	25	5	4	− 13	− 4	0
I	70	13	3	—	—	—	13	6
H	—	0	2	5	4	7	34	39
Na	0	—	—	− 44[1]	51	—	78	96

It is to be noted that :

For hydrogen the values stand in the same order as for sodium, except that the difference of thermal effect due to combination with oxygen and chlorine is reduced, and would even be reversed if the heat of solution of hydrochloric acid (17) were not taken into account, in which case the value for chlorine would be only 39 − 17 = 22.

For phosphorus the value for combination with oxygen is actually the greater, and for sulphur the excess reaches a maximum.

Going further to the right, a second characteristic appears, since the heat of combination with hydrogen increases, becoming equal to that for combination with chlorine, in the case of carbon and sulphur, and exceeding it for nitrogen, oxygen, and chlorine ; so that at the extreme right, for chlorine the relative magnitude of the quantities of heat is reversed in almost every respect : this is shown by

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[1] Refers to formation of the silver compound $(Ag_2C_2) = − 87.15$, *Centralblatt*, 1899, 11. 583.

Fig. 4, in which the heat values for sodium and chlorine, on combination with sulphur, oxygen, chlorine, iodine, hydrogen, and sodium, are represented by the lines I and II.
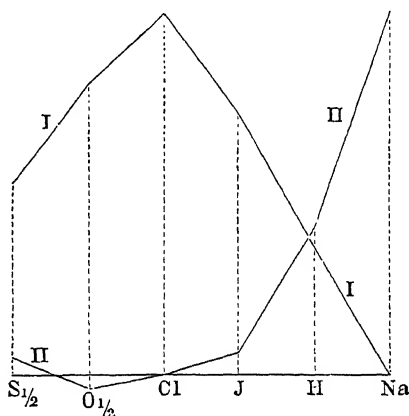
Fig. 4.

It should be added that the contrast which we have seen to exist between sodium and chlorine in their facility for associating with electricity, i. e. for forming ions, reappears in these thermal values, and that the evolution of heat in the combination of two elements goes hand-in-hand with their facility for associating with opposite electrical charges. One would be inclined from this to think that in the more marked phenomena of affinity electricity plays the leading rôle, and that whilst a pair of similar atoms such as the chlorine in the chlorine molecules are held together essentially by their direct mutual action, in sodium chloride, on the other hand, the sodium and chlorine hold fast to a charge of negative and positive electricity respectively, which then, by their mutual attraction, unite the whole.

Again, the two opposite indications of affinity depending on electric charges are best seen in univalent elements, and especially those with small atomic weights, and large atomic volumes, i. e. when the action of mass is smallest.

3. *Tendency to Self-combination*[1].

Another characteristic feature of affinity is the greater or less tendency of similar atoms to combine together. In univalent atoms this action is obviously limited to the formation of diatomic molecules, which appears not to occur amongst the metals (Part II, p. 60), but to be general amongst the metalloids, although the halogen molecules consisting of two atoms break up at high temperatures (Part II, p. 26).

The tendency can show itself over a wider area in the case of the multivalent elements, since the molecules of the elements themselves may consist of more than two atoms, and compounds too may contain several similar atoms attached together. Here again it is essentially among the non-metals that this tendency is found, and that in very varying degree.

The tendency to self-combination is much the most marked in the case of carbon; not only are compounds in homologous series up to thirty and more carbon atoms arranged in order known, but this accumulation does not cause the least indication of reduced stability. And free carbon is, according to pp. 54 and 71, most probably composed of polyatomic molecules.

Next comes silicon, although far behind carbon, since e. g. the newly discovered silicomesoxalic acid [2]

$$HO_2Si . SiO . SiO_2H$$
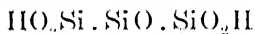
with only three silicon atoms arranged in series, is converted by soda with evolution of hydrogen, into silica, in which self-combination of silicon cannot be assumed.

The property in question is found in sulphur to a certain extent, e. g. potassium pentasulphide

$$KSSSSSK \text{ or } \begin{array}{c} S \\ \diagdown \\ S \end{array} \!\!\! S \!\!\! \begin{array}{c} S-K \\ \diagup \\ S-K \end{array}$$
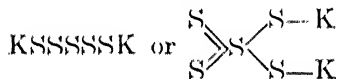
is capable of existence; but the corresponding acid gives

[1] Van 't Hoff, *Ansichten über organische Chemie*, ii. 240.
[2] *Berl. Ber.* 32. 1114.

off sulphur.   Moreover the density of sulphur vapour
(Part II, pp. 26, 60) indicates a composition S_8, which how-
ever changes at higher temperature into S_2.

In oxygen the tendency to self-combination is further
reduced, and even the compounds that contain two con-
nected oxygen atoms are not very stable, whilst free oxygen
when triatomic, in the form of ozone, is well known to be
explosive.

It may be remarked finally that the tendency to self-
combination is so far connected with the positive or nega-
tive character, that it appears only in the intermediate
elements.   The table, p. 93, shows this clearly; left and
right are sodium and chlorine, strong positive and nega-
tive, of which the former occurs in monatomic molecules,
whilst the latter decomposes into such on heating : then
come hydrogen and oxygen, which are quite stable in the
diatomic form, and of which oxygen is known as triatomic ;
then follow nitrogen and phosphorus, of which the former
is known e. g. as azoic acid N_3H with three atoms united
together, whilst phosphorus occurs as tetratomic molecules.
In the middle are sulphur and carbon.

As is usually the case, this effect of affinity is strongest
for small atomic weight, as is seen in the specially strong
tendency of carbon to combine with itself, and in the rela-
tive ease with which the diatomic molecules of iodine
break up as compared with the stability of chlorine in this
respect.

4. *Velocity of Reactions* [1].

The elements show characteristic differences in the very
diverse facility with which reactions occurring in their
compounds take place.   Carbon in particular is distin-
guished by its striking ' inertia ' in this respect.

Even in the simplest cases, on going into combination
with other elements this inertia of carbon is apparent, in
the first place, in its high temperature of inflammation.

[1] *Ansichten über organische Chemie*, ii. 224. 244.

Although very strong forces favour the oxidation, graphite is so protected from them that it can be used for making crucibles, whilst the imflammability of diamond was only discovered very late, for the same reason.

On the other hand compounds of carbon are known, such as acetylene, that break up with a large evolution of heat, so that strong forces are tending to decompose them, and yet possess a relatively, often strikingly great stability. In the same way it is amongst the carbon compounds that isomerism is observed, since that implies that less stable forms are capable of continued existence [1]. Thus all the hydrocarbons of the formula C_6H_{14} can be prepared and kept, whilst among inorganic compounds of the formula PO_3NH_6, e. g. only two ammonium phosphates and hydroxylamine hypophosphite can be obtained, and of these the latter slowly decomposes.

Thus, in consequence of this inertia, it is the chemistry of the carbon compounds that is the region of slow reactions, and consequently of measurements of velocity; finally we may recall that the most important principle in determining constitution (Part II, p. 87) depending on the fact that in a reaction the least number of linkages possible is broken is the immediate consequence of the inertia here mentioned.

It cannot be overlooked that this last peculiarity in the phenomena of affinity is also to be brought into connexion with the positive or negative character. If that is pronounced, then as seen on p. 91 ionization, i. e. breaking up and loosening is favoured, which leads in salts, &c., to instantaneous reaction. In carbon which stands just in the middle (p. 93) and is neutral, this cause favouring reaction is wanting.

SUMMARY.

The preceding four characteristics of the elements in regard to affinity may be brought under a single point of

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[1] Hantzsch, *Ann. der Chemie*, 292. 340.

view. For this we choose the so-called positive or negative character of the elements to start with, and define this as tendency to combine with positive or negative electricity. The extreme positive and negative elements, such as sodium and chlorine, then show the strongest indications of affinity, which suggests the assumption that in the chemical combination the opposite electrical charges can act on one another. Then the intermediate elements, such as carbon, which are neither decidedly positive nor negative, often show a tendency to combine with themselves which is wanting in the extreme members. The second consequence of the tendency to combine with electricity is therefore the appearance of free atoms with electric charges, ions, in solvents which e. g. weaken the electric attraction, and show a high dielectric constant, such as water: this breaking up or loosening again produces a facility for reaction which the compounds of the intermediate elements do not possess, and in carbon compounds the opposite effect is seen in their characteristic inertia in reaction. All these phenomena of affinity are most marked when the atomic weight is small and the atomic volume large, and consequently the density small.

B. Affinity of the Elements in more Complex Compounds.

After what has been given in the foregoing on the characteristic effects of affinity in simple compounds, the corresponding phenomena in more complex derivatives must be studied. First the additive character of the heat of formation is to be noted, and secondly, the composition of explosive compounds.

1. *Additive Character of the Heat of Formation.*

It was Thomsen [1] in the first place who attempted to reduce the thermal phenomena of organic chemistry to their elements in the simple formation and destruction of

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[1] *Thermochemische Untersuchungen,* iv. 237.

atomic linkages. There are some points to be borne in mind in applying thermal data for this purpose.

The first is that if the reaction studied in the calorimeter is accompanied by a change of volume, and is not performed in a bomb, a part of the thermal effect is due to external work, so that the value obtained will be too high if the reaction takes place with contraction. The correction to be made on this account is very simple, since only the work done in changing the volume of a gas has to be considered, the changes in the liquid and solid phases being negligible in amount. Take for example the combustion of carbon monoxide

$$2\,CO + O_2 = 2\,CO_2.$$
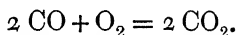
Under constant pressure this is accompanied by a contraction, since three molecules are converted into two. The work thus converted into heat is per kilogram-molecule

$$APV = 2\,T \text{ calories};$$

so that in the foregoing case in which $2(12+16) = 56$ kilograms of carbon monoxide are burnt at ordinary temperature $(17°)$

$$2(273+17) = 580 \text{ calories}$$

of heat are gained by the contraction, and are consequently to be subtracted from the heat of combustion to obtain the number relating to the actual chemical process. If as the data here used and to be used, we employ the gram-molecule, then for each molecule of gas that disappears 0.58 calories must be subtracted, for each molecule formed, that amount is to be added.

A second point of much greater magnitude in effect is the state of aggregation at the moment, since alteration of it is accompanied by a very considerable thermal effect, e.g. the solidification of water evolves $0.08 \times 18 = 1.44$ calories, and its evaporation absorbs $0.6 \times 18 = 10.8$. In the numerical comparison Thomsen dealt with the gaseous state. The direct method of judging the additivity, by starting from the heat of formation of simple binary com-

pounds, is not available in the region of organic chemistry on account of the involatility of carbon, hence we are driven to indirect methods.

In the first place, isomers have nearly the same heat of combustion, e. g.

propyl alcohol 498·6,   isopropyl alcohol 493·3 ;

whilst the failure of this equality in the case of acetic acid,

acetic acid 225·4,   methyl formate 248·1,

is partly to be referred to the double molecules existing in the vapour, in whose dissociation heat is absorbed, and the heat of combustion accordingly reduced.

Equal differences in composition correspond approximately to equal differences in heat of combustion, such as those shown in a homologous series (the hydrocarbons are burnt in the form of gas or vapour, the water collected liquid) :

CH_4	C_2H_6	C_3H_8	C_4H_{10}	C_5H_{12}
211·9	370·4	529·2	687·2	847·1

difference 158·5,   158·8,   158,   159·9.

Passing now from heat of combustion to heat of formation, by means of the law that the heat of a reaction is the sum of the heats of formation of the products diminished by the corresponding sum for the reacting substances, we get from the heat of combustion of CH_4 :

$$CH_4 + 2O_2 = CO_2 + 2H_2O + 211·9 \text{ calories,}$$
$$211·9 = (C.O_2) + 2(H_2.O) - (C.H_4),$$

in which $(C.O_2)$ and $(H_2.O)$ stand for the heat evolved in the formation of 44 grams of carbon dioxide and 18 grams of water from the elements : these are (carbon as diamond)

$$(C.O_2) = 94·3,   (H_2.O) = 67·4,$$

so that

$$(C.H_4) = 94·3 + 134·8 - 211·9 = 17·2,$$

or the formation of 16 grams of methane from diamond and

hydrogen causes an evolution of 17·2 calories.   In the same
way for the whole series we have

CH_4	C_2H_6	C_3H_8	C_4H_{10}	C_5H_{12}
17·2	20·4	23·3	26·0	28·8

$14·3 + 2·9\,n = 17·2$ 20·1   23·0   25·9   28·8.

We can now give a purely empirical expression to the
additive character by deducing from these numbers a value
for carbon and one for hydrogen.   Since the mean dif-
ference is

$$CH_2 = 2·9,$$

we have

$$H_2 = CH_4 - CH_2 = 17·2 - 2·9 = 14·3$$
$$C = CH_2 - H_2 = 2·9 - 14·3 = -11·4,$$

so that

$$C_nH_{2n+2} = -11·4\,n + (n+1)\,14·3 = 14·3 + 2·9\,n.$$

In this expression, however, although it reproduces the
above data, a very important point is overlooked, since
a priori the heat of formation cannot be expected to depend
simply on the components but rather on their mode of
combination, as is indicated by any heat of reaction, since
according to our notions only the mutual linkages are
changed.

Taking this into account, the formation of the above
hydrocarbons is to be regarded as a combination of carbon
with carbon (C—C) and carbon with hydrogen (C—H), and
assuming a constant value for the latter we get from the
heat of formation of methane

$$4\,(C—H) = 17·2, \text{ so that } (C—H) = 4·3.$$

Hence for pentane

$$4\,(C—C) + 12\,(C—H) = 28·8 \text{ so that } (C—C) = -5·7,$$

whence for C_nH_{2n+2} :

$$(n-1)\,(C—C) + (2n+2)\,(C—H) = -5·7\,(n-1)$$
$$+ 4·3\,(2n+2) = 14·3 + 2·9n.$$

Although the previous expression and the experiments
agree with this, it needs modification in case of combina-

tion between these two elements in which double or triple linkages are involved.

For ethylene $H_2C = CH_2$

$$[C_2 . H_4] = -10,$$

the above expression leads to $2 \times 2 \cdot 9 = 5 \cdot 8$. If, however, we change it on account of the double carbon linkage, putting

$$(C = C) = -10 - 4(C\text{—}H) = -10 - 4 \times 4 \cdot 3 = -27 \cdot 2,$$

all the hydrocarbons with double linkage are brought within the domain of the formula.

In the same way for triple linkages, we have from the value for acetylene $HC \equiv CH$

$$[C_2 . H_2] = -53 \cdot 2,$$
$$(C \equiv C) = -53 \cdot 2 - 2(C\text{—}H) = -53 \cdot 2 - 2 \times 4 \cdot 3 = -61 \cdot 8.$$

The correctness of the expression so obtained may be tested by a provisional determination of constitution : we will choose benzene as example.

For the isomer dipropargyl, with the constitution

$$HC \equiv C . CH_2 . CH_2 . C \equiv CH,$$
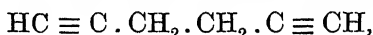
it is found that

$$[C_6 . H_6] = -113 \cdot 4,$$

with which calculation gives good agreement

$$2(C \equiv C) + 3(C\text{—}C) + 6(C\text{—}H) = -2 \times 61 \cdot 8 - 3 \times 5 \cdot 7$$
$$+ 6 \times 4 \cdot 3 = -114 \cdot 9.$$

For benzene the heat of formation is

$$[C_6 . H_6] = -17 \cdot 1,$$

and since $6(C\text{—}H) = 6 \times 4 \cdot 3 = 25 \cdot 8$, there remains for the carbon linkages

$$-17 \cdot 1 - 25 \cdot 8 = -42 \cdot 9.$$

If the linkage is alternately single and double we should expect

$$3(C = C) + 3(C\text{—}C) = 3(-27 \cdot 2 - 5 \cdot 7) = -98 \cdot 7,$$

but nine simple bonds, as in the centric formula (Part II, p. 96) would give

$$9\,(C—C) = -9 \times 5 \cdot 7 = -51 \cdot 3,$$

which comes fairly near to the observed value.

The relations are not quite exact, and it is not to be expected they should be, for, as will be seen later, the presence of one element affects the affinity of another, e.g. the substitution of each new chlorine atom in methane produces a lessened heat effect; the numbers are as follows:

CH_4	CH_3Cl	CH_2Cl_2	$CHCl_3$	CCl_4
17·2	19·2	24·6	20·9	17·8

Difference $+2$ $+5 \cdot 4$ $-3 \cdot 7$ $-3 \cdot 1.$

2. *Constitution of Explosives.*

Explosives are characterized by the fact that they cause a sudden increase of pressure. If a chemical reaction is concerned in it, it is necessary that it should take place rapidly and with a large increase of volume and temperature. (See Part I, p. 251.) The essential factors in this process were discussed, and attention was paid on p. 253 to the velocity of explosion. We shall restrict ourselves to considering the pressure, and especially to the part played by evolution of heat, noting that the pressure theoretically depends on the following relation:

$$P = \frac{V_2}{V_1}\,(1 + at),$$

where V_1 and V_2 are the volumes at $0°$ and one atmosphere before and after the explosion, and t the rise of temperature caused by the production of heat at constant volume.

Since $\dfrac{V_2}{V_1}$ can only be large when the products of explosion are gaseous, two categories must be distinguished in regard to this effect, according as the factor $\dfrac{V_2}{V_1}$ is of

importance or not. The first includes explosive materials that are solid or liquid, the latter those that are gaseous. In the former group, which includes gunpowder, the factor $\frac{V_2}{V_1}$ alone is something like one thousand, in the latter, e. g. oxyhydrogen mixture, mostly near unity, and may be less, as in the instance mentioned where it is two-thirds ; hence in the former case the pressure may be thousands of atmospheres, in the latter from a few up to twenty, mainly on account of the factor $(1 + at)$. The explosives used in practice therefore belong exclusively to the first category, i. e. are solids or liquids which form gases with a considerable evolution of heat.

We may now go over the various bodies in question, with reference to their composition and the connexion between constitution and explosibility, beginning with the simplest, we get the following scheme :

    (*a*) Simple explosives.

    (*b*) Explosive mixtures.

    (*c*) Practical explosives.

(*a*) *Simple Explosives.*

First, we will bring together the simpler bodies that are capable of reaction with evolution of heat, whether actual explosion takes place or not. The main condition for an explosion is then given, and it has only to be considered what conditions bring it to pass.

The first element to consider which plays such a part is ozone (O_3), which, in the liquid state, is capable of explosion with formation of oxygen (O_2) with an evolution of heat that amounts to 36 calories for the gas, per 48 grams (O_3) of material.

Next in simplicity come the binary compounds, of which a list is appended, with the heat of formation of each from its elements :

Hydrogen compounds:

$$(Sb . H_3) = -82, \qquad (As . H_3) = -44, \qquad (H_2O . O) = -23.[1]$$

Oxygen compounds:

$$(N . O) = -22, \qquad (Cl_2 . O) = -18.$$

Nitrogen compounds:

$$(N_3 . H) = -62,[2] \qquad (N . Cl_3) = -39, \qquad (N . S) = -32,$$
$$(N . Se) = -43.$$

Carbon compounds:

$$(C_2 . H_2) = -53, \qquad (C . S_2) = -22, \qquad (C_2 . N_2) = -71,$$
$$(C_2 . Ag_2) = -87.[3]$$

Explosion occurs under different conditions for the different substances, for most solid and liquid compounds, by a mechanical shock, such as NCl_3, N_3H, C_2H_2, &c.; by a very violent shock such as may be produced by an explosion, say of silver fulminate, in the case of C_2N_2, As H_3 and C_2H_2 as gases; by heat for Cl_2O, O_3, H_2O_2; by sudden compression, i.e. combined heat and shock, in the case of N_2O;[4] and it is well known that light and electric sparks will, under some circumstances, determine an explosion.

We may apply the foregoing data to obtain a first insight into the constitution of explosive substances, and show that certain atomic combinations produce the explosive character.

Combination of similar atoms often plays a part in the elements, resulting in a strained position. If the atoms are univalent, such a combination cannot occur in the derivatives. On the other hand, in diatomic oxygen we have the appearance of a complex

$$O—O$$

that leads to easy breaking up. The table above contains such cases in ozone and hydrogen peroxide:

[1] Heat of formation from oxygen and water.
[2] *Berl. Ber.* 32. 1399.   [3] *Centralblatt*, 1899, 11. 583.
[4] Berthelot, *Matières explosives*, I. 114.

$$
\begin{array}{c}
O \\
\triangle \\
O\!-\!O
\end{array}
\qquad \text{and} \qquad
\begin{array}{c}
H \quad H \\
| \quad | \\
O\!-\!O
\end{array}.
$$

In all superoxides, such as acetyl superoxide,

$$(C_2H_3O)\ O\!-\!O\ (C_2H_3O),$$
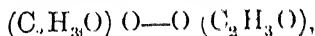
the same easy decomposition is observed.

In trivalent nitrogen it is especially the group

$$N = N,$$

that breaks up with large evolution of heat.   Among the data given above we have the example of

$$
\begin{array}{c}
N = N \\
\diagdown \quad \diagup \\
N \\
| \\
H
\end{array}
$$
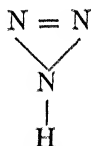
In the same way the diazo-bodies are explosive, e.g. diazo-benzene nitrate

$$C_6H_5N = NONO_2.$$
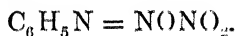
In quadrivalent carbon it is the combination

$$C \equiv C,$$

which is the essential cause of explosion, and has already, on p. 102, been shown to involve a large absorption of heat.   Table, p. 105, contains two such bodies

$$HC \equiv CH \quad \text{and} \quad AgC \equiv CAg.$$
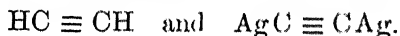
The explosive character depending on this has been found also by Baeyer[1] in polyacetylene derivatives, such as diacetylene di-iodide C_4I_2.

The combinations of two elements that cause explosibility are mainly those given in the table above, and there remain to be mentioned only a few important, more complex groups that are connected with them.

The strained position in combination of nitrogen and oxygen which showed itself in the table in the negative

heat of formation of nitric oxide, recurs in the nitro-deri-vatives and nitrates, such as nitromethane and methyl nitrate

$$H_3CN\!\!\ll_O^O \qquad \text{and} \qquad H_3CON\!\!\ll_O^O$$
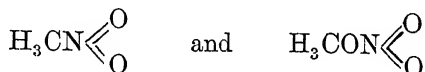
which contain the nitro group NO_2.

The strained position of oxygen in combination with chlorine shows itself in the explosive character of the chlorates and perchlorates, which all contain the chlorine-oxygen linkage.

It may be added that the combination of carbon and nitrogen which causes cyanogen to be explosive, exists also in the true nitro-compounds, such as nitromethane. The list of explosive linkages is therefore:

O—O,	N=N,	C≡C,	
H—Sb,	H—As,	O—N,	O—Cl,
N—Cl,	N—S,	N—Se,	
C—S,	C—N,	C—Ag.	
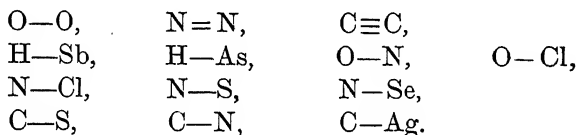
(b) *Explosive Mixtures.*

Two elements. In what precedes, the cause of explosive character was regarded as a strained atomic combination, the freeing of which produces a sudden reaction. In the reverse way a mixture may lead to explosion if it affords opportunity for new atomic combinations. Starting again with the simplest case, this will be a mixture of two elements which can combine with large evolution of heat and yield gaseous products, especially if the elements are taken in the solid or liquid state. The essentials are thus, miscibility, evolution of heat, initial solid or liquid state, and production of gas. With regard to evolution of heat, choice may be made by means of the table on p. 93. For metals the highest values are obtained by combination with fluorine, chlorine, oxygen, and sulphur; these, how-

ever, need not be considered on account of involatility of their products. Of the non-metals which alone need be considered, the following mixtures rank first:

$$(H_2.O) = 69, \quad (H.Cl) = 22, \quad (H.F) = 37, \quad (C.O_2) = 97.$$

Actually these include two known explosive mixtures, viz. oxygen and hydrogen, and chlorine and hydrogen. A mixture of fluorine and hydrogen, on the other hand, passes of its own accord into hydrofluoric acid, while carbon and oxygen are not miscible.

The other factor conditioning practical applicability—initial, solid, or liquid state—is wanting in the four preceding cases, but may be arrived at by liquefying the gases; this can be accomplished in the case of carbon and oxygen by mixing finely-divided carbon with liquid air. This yields an actually available explosive [1].

Three elements. By suitably combining two conditions, strain in linkages actually existing, and formation of new linkages with strong affinity, the effectiveness of explosive mixtures may be increased; this may be done by choosing three elements, A, B, and C, such that, e.g. the compound of A and B is decomposed with a large evolution of heat, whilst that of A or B with C is formed with a large evolution of heat. Let us consider the possibilities of this with the aid of the former data.

Of cases in which C combines with one of the elements A and B with a large evolution of heat, we find

$$NO + H_2 = N + H_2O, \qquad W = 69 + 22 = 91,$$
$$2 N_3H + \tfrac{1}{2} O_2 = 3 N_2 + H_2O, \qquad W = 69 + 2 \times 62 = 193.$$
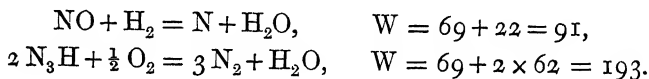
Of cases in which C combines with both the elements A and B with a large evolution of heat, we find

$$CS_2 + 3 O_2 = CO_2 + 2 SO_2, \qquad W = 97 + 2 \times 71 + 22 = 261,$$
$$C_2H_2 + \tfrac{5}{2} O_2 = 2 CO_2 + H_2O, \qquad W = 2 \times 97 + 69 + 53 = 316.$$
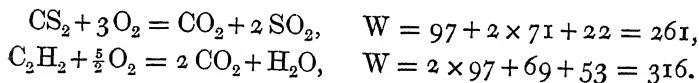
[1] Bujard, *Leitfaden der Pyrotechnik*, 1899, p. 189.

If ozone is used instead of oxygen the effect is markedly increased :

$$CS_2 + 2\,O_3 = CO_2 + 2\,SO_2, \qquad W = 261 + 2 \times 36 = 333,$$
$$C_2H_2 + \tfrac{5}{3}\,O_3 = 2\,CO_2 + H_2O, \qquad W = 316 + \tfrac{5}{3} \times 36 = 376,$$
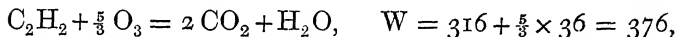
so that a liquid mixture of acetylene and ozone might be expected to form one of the most effective explosives.

Four elements. Yet another possibility may be added to the above, since two pairs of elements in the form of compounds AB and CD, which each decompose with evolution of heat, might be so chosen as to yield two, AC and BD, with the largest possible heat of formation. An example of this may be derived from what precedes
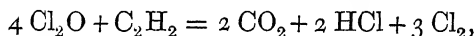
$$4\,Cl_2O + C_2H_2 = 2\,CO_2 + 2\,HCl + 3\,Cl_2,$$
$$W = 2\,(22 + 97) + 4 \times 18 + 53 = 363.$$

(c) *Practical Explosives* [1].

The materials remarked on above as being suitable on thermal grounds, some of which exceed in effect the explosives so far made use of, are nevertheless often unsuitable on account of the great danger in handling them, so that for practical purposes we must add safe handling as a further condition. We will consider from this point of view, solid and liquid mixtures, and more complex compounds in order.

(a) *Solid mixtures.* (*Black gunpowder.*) Solid mixtures are usually fairly safe, because, in the solid state, the homogeneity of the mixture, and the contact between the components, are never complete ; the former may be improved by fine grinding, the latter by compression, or preliminary fusion and solidification. The most important substance belonging to this category is ordinary gunpowder, made of sulphur, carbon, and nitre. The me-

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chanism of the explosion is explained by the fact that
in nitre

$$\begin{matrix} O \\ \diagdown \\ O \end{matrix}\!\!\gg\!\!N\!-\!O\!-\!K,$$
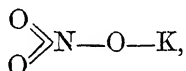
the oxygen combined with nitrogen is, according to p. 105,
in a strained position ; it is destined to combine with the
carbon, which, according to p. 107, is among the first in
point of evolution of heat of those elements that yield
gaseous products.   The potassium is then free to combine
with the element with which its heat of combination is
greatest, sulphur, the reaction taking place in the follow-
ing way :

$$2\,KNO_3 + S + 3\,C = 3\,CO_2 + K_2S + N_2.$$
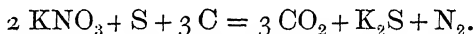
This expression corresponds with the composition actu-
ally used : but in consequence of incomplete mixture other
reactions occur locally.

(β) *Liquid mixtures.*   Besides the disadvantage just
mentioned, solid mixtures suffer from another, in that the
reaction on account of imperfect mixture and contact
cannot go fast, causing only a gradually propagated com-
bustion at a few metres per second, instead of the explo-
sive wave (Part I, p. 253) travelling at more than 1000
metres.   The danger in handling liquid explosives thus
arising may be avoided in several ways.   At the present
moment such a mixture is used e.g. in carbon and liquid air,
and perhaps the new resources in low temperatures and
liquefied gases will make available much better mixtures
still, such as those mentioned on p. 108.   It may be added
that, if one of the components contains carbon, the inertia
of the affinity of carbon (p. 97) is favourable to safety,
although it does not hinder the development of an explo-
sive wave.   Thus a mixture of ether with peroxide of
hydrogen up to 70 per cent. can be kept entirely without
danger, and is used by dentists, although it is undoubtedly
capable of violent explosion.

(γ) *More complex compounds.*   (*Smokeless gunpowder.*)

The technique of explosion, which started with the employment of dynamite, is based, theoretically, on bringing together the explosive groupings discussed above, not, however, by mixture, but by the much more intimate process of chemical combination; in other words the nitro group which, in black powder present in the nitre, is mixed with carbon, in dynamite and similar bodies is more or less loosely combined with carbon.

In inorganic chemistry instances of a similar kind are found in the ammonia salts that readily give off oxygen, such as the perchlorates. These have no practical application, just because on account of their facility of reaction, explosive inorganic compounds are unsafe to handle. But in organic compounds the inertia of the carbon combination allows of the accumulation of a very great amount of latent energy with relatively little danger.

In the first place then come the nitrates, or so-called nitro bodies which contain the group

$$-C-O-N\diagup\diagdown{\!\!\!\!\!\!\!\!}{O \atop O}$$
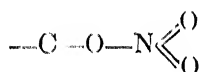
once or more, as in dynamite, which is fine sand mixed with nitroglycerine

$$H_2C(ONO_2)\,CH\,(ONO_2)\,CH_2\,(ONO_2),$$
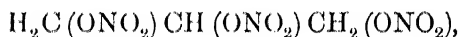
in gun cotton which contains a longer carbon chain $C_{12}H_{14}(NO_3)_6O_4$, in blasting gelatine, a solution of gun cotton in nitroglycerine, and in the other so-called smokeless powders.

The cause of explosiveness is obvious; carbon and hydrogen are presented to the oxygen, already in a strained position on account of its combination with nitrogen. The combination will therefore be most effective if the carbon and hydrogen are just sufficient to combine with the oxygen. Nitrates of monatomic alcohols contain an excess of hydrogen

$$H_3CONO_2 = CO_2 + H_2O + H.$$

In diatomic glycol the quantity is just sufficient

$$H_2CONO_2H_3CONO_2 = 2\,CO_2 + 2\,H_2O.$$
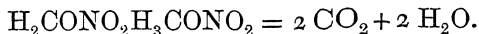
In glycerine the quantity is already slightly too little and in gun cotton still more so, so that the highest point is reached in glycol nitrate.

Still better, on theoretical grounds, are suitably chosen true nitro-compounds, containing the group

$$-C-N\mkern-6mu\begin{array}{l}O\\O\end{array}$$
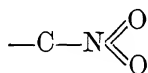
These have the advantage of the nitrates in possessing oxygen in a strained position ; but also the carbon which, in the former case, was partly combined with oxygen is now combined with nitrogen, which, according to the data for cyanogen, on p. 105, also implies a strain. If, again, we choose the most suitable body, that in which the oxygen is just sufficient for the carbon, we shall find it in dinitro-acetylene, which is not at present known

$$NO_2CCNO_2 = 2\,CO_2 + N_2,$$
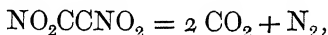
which has, moreover, the advantage of the endothermic triple linkage. Somewhat less suitable, for these reasons, is the equally unknown hexanitrobenzene, although here again the oxygen is just sufficient for combustion of all the carbon. Trinitrobenzene is again somewhat behind the preceding

$$C_6H_3(NO_2)_3 = 6\,CO_2 + 3\,H,$$
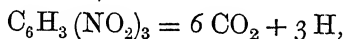
of the trinitrobenzenes, picric acid ($1 \cdot 3 \cdot 5\ C_6H_3(NO_2)_3$) is used as an explosive under the names of lyddite and melinite. It is of importance for that purpose, previously to melt the solid substance in order to give it a suitable inner structure and explosiveness.

§ 2. The Influence on Elements already present in a Compound exerted by Elements introduced.

The influence which the introduced element exerts on the behaviour of a compound is seen, in the first place, in reactions which cause changes in the linkages of that element : these have been considered in the previous paragraphs. The introduction has, however, a further influence which appears if in the molecule other linkages can be broken, and in general this influence falls off with distance. The influence is most clearly shown in the region of organic chemistry, and may be brought under certain rules though mostly only qualitative ; of these many are grouped round the leading fact that an element communicates its electro-affinity to the atomic group in which it appears, and consequently raises or lowers its tendency to associate with positive or negative electricity, with all the consequences already described ; commonly the result of this is a more or less marked positive or negative character in the group. We will first deal with this point of leading importance, which is to be traced essentially in the matter of equilibrium, afterwards bringing together the further specific influences which appear principally in changes of velocity.

A. Introduction of the Electro-affinity, i.e. of Positive or Negative Character, into the Group into which an Element enters.

In the first place, since we are dealing essentially with 'organic compounds, carbon is fairly indifferent towards positive or negative electricity, i. e. it shows little tendency to go into the ionic form. Hence the negative or positive influence of associated elements is the more completely felt. If this is negative it causes formation of positive H-ions, i. e. of acid character, and reduces the tendency to form negative OH-ions, i. e. basic character, but only, of course, if hydrogen or hydroxyl is contained in the element

in question. Positive influence acts in the opposite direction. Hence these opposing influences have first to be dealt with in the case of each element.

1. *Influence of Positive Elements.*

(a) *Influence of Hydrogen.*

(*o*) *Hydrogen affects acidity.* Beginning with the simplest case, it is first to be noted that the influence of hydrogen in question is appreciable in carbon itself. The element named has a certain tendency to combination with the metals: the compounds with iron (in cast iron) and nickel are quite stable bodies which are decomposed by acids, but not by water: and the compounds with the lighter metals, as calcium (carbide), can be produced directly, but are decomposed by water with formation of acetylene. It is different when the carbon valencies are as far as possible saturated with hydrogen, as in methyl: the tendency to combination with the metals is then so far reduced that, e. g. zinc methyl is instantaneously decomposed by water, and indeed spontaneously inflammable, whilst compounds with the light metals are so difficult to arrive at that they have not yet been prepared.

In more complicated cases the same thing is observed; compare compounds that contain the groups:

$HC \equiv C$, $HC = CH$, $H_2C = CH$, and $H_3C—CH_2$.
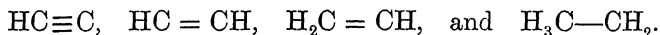
In the first the tendency to take up metals is so far marked that the acetylene compounds (acetylides) show a weak acid character, and give precipitates containing metal, with silver oxide and cuprous oxide. So do acetylene and propargyl alcohol, forming

$Ag—C \equiv C—H$ and $Ag—C \equiv C—CH_2OH$.
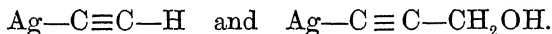
This tendency disappears in the three other groups mentioned, which are richer in hydrogen; only in the group $HC = CH$ is an influence in the same direction observed [1].

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[1] Henrich, *Centralblatt*, 1899, **11**. 701.

After dealing with the tendency of hydrogen combined with carbon to be replaced by metals, we may take hydrogen combined with oxygen, i. e. hydroxyl. Here, in accordance with the facility metals have for combination with carbon the tendency to metallic combination is far more marked. This tendency, however, to form 'metallic alcoholates' is in a high degree dependent on the hydrogen otherwise contained in the compound, and diminishes with increase of the latter. Taking the extreme cases phenol and hexyl alcohol

$$C_6H_5OH, \qquad C_6H_{13}OH,$$
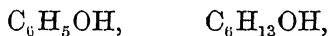
the predominance of acid character in phenol is marked by the name 'carbolic acid.' Actually potassium phenolate, C_6H_5OK, can be prepared from potash like a salt according to the equation

$$C_6H_5OH + KOH = C_6H_5OK + H_2O,$$
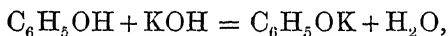
whereas for hexyl alcohol, potassium is needed

$$C_6H_{13}OH + K = H + C_6H_{13}OK.$$
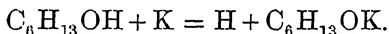
This again is connected with the fact that the metallic derivatives in question are hydrolytically dissociated by water, in the first case slightly, in the second strongly, and that the constant governing the equilibrium

$$XOK + H_2O \rightleftharpoons XOH + KOH$$
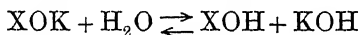
is here to be regarded as a measure of the influence of hydrogen. For potassium phenolate this can be numerically determined [1] by measuring the velocity with which methyl acetate is saponified in solution with the phenolate, as this allows of calculating directly the amount of potash. It was found that:

0·0962 normal solution at 24·1° was 3·05 % hydrolyzed,
0·0195   „   „   24·1°   „   6·69 %   „

whilst hexyl alcohol was hydrolyzed to the extent of more than 90 %.

[1] Shields, *Zeitschr. f. Phys. Chemie*, **12**. 175.

Consider finally bodies containing carboxyl, in which the facility for introducing metal in the hydroxyl group, is again increased by the presence of the new atom of oxygen in the carboxyl group

$$O = C - O - H.$$
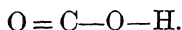
The acid character thus arising changes markedly in strength under the influence of the combined hydrogen, and in the sense expected. As previously (Part I, p. 135) the dissociation constant may be taken as a measure of the strength; we then get in the extreme cases

Benzoic acid C_6H_5COOH $K = 0.006,$
Heptylic acid $C_6H_{13}COOH$ $K < 0.00145,$

whilst for valerianic acid $(C_5H_{10}O_2)$ $K = 0.00161,$ and for hexylic acid $(C_6H_{12}O_2)$ $0.00145.$

(β) *Hydrogen intensifies basicity.* Since basic character is due to the possibility of forming hydroxyl ions, the property of hydrogen in question can only be studied in organic compounds of a basic character, i.e. the alcohols. Actually it appears that the tendency of alcohols to esterification, in which their basic character is shown, is modified in the expected manner by hydrogen. Again, taking extreme cases, and choosing as appropriate measure of the tendency to esterification not the velocity but the limit reached we have

C_6H_5OH $8.6 \%,$ $C_6H_{13}OH$ $67.3 \%,$

i.e. phenol heated to 144° for a sufficient time with the equivalent amount of acetic acid combined to the extent of 9 per cent., but primary normal hexyl alcohol to the extent of 67 per cent.

It is possible to go further in this case, with the aid of the more complete investigation of Menschutkin, and not only to demonstrate the influence of hydrogen in general, but to show that the hydrogen which is nearest to the hydroxyl group is the most effective; the average limit was found to be for

H_3COH	XH_2COH	$YXHCOH$	$ZYXCOH$
70	67	60	10 $\%,$

in which lies a means of discriminating methyl alcohol, the only one in which three hydrogen atoms are carried by the carbon atom to which the hydroxyl is attached, primary, secondary, and tertiary alcohols.

(γ) *Examples from Inorganic Chemistry.* The two influences of hydrogen we have described are not confined to organic chemistry; a striking example may be found in the inorganic region in the compounds of hydrogen with nitrogen, ammonia, hydrazine, and Curtius' azoic acid

$$NH_3, \qquad N_2H_4, \qquad N_3H.$$
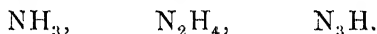
Both influences of hydrogen are to be seen, on the one hand as increase of basic properties, shown by the two first compounds in the form of hydrates, of which ammonia is the stronger; on the other, the decrease of acidity, since azoic acid is converted by addition of hydrogen into the base hydrazine.

(b) *Influence of the Light Metals, especially Sodium.*

(a) *Examples from Organic Chemistry.* The influence of metals is like that of hydrogen, inasmuch as acidity is diminished by introduction of a metal, apart from the saturation which follows the replacement of the hydrogen atom. In organic chemistry this is seen, e.g. in the malonic esters:

$$CO_2C_2H_5CH_2CO_2C_2H_5,$$

which form a metal derivative with sodium ethylate.

$$CO_2C_2H_5CHNaCO_2C_2H_5.$$

The question why both the hydrogen atoms of the CH_2 group, since they are similarly placed, are not replaced by sodium, giving

$$CO_2C_2H_5CNa_2CO_2C_2H_5,$$
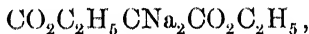
is answered by the fact that the acid character of the compound is depressed by introduction of a metal, and more by sodium than by the hydrogen which is simultaneously expelled.

(β) *Examples from Inorganic Chemistry.* The same effect of the introduction of metals is seen in the progressive saturation of polybasic acids such as phosphoric, in which the successive evolutions of heat diminish notably.

$PO_4H_3 + NaOH$ 14·8, $+ NaOH$ 12·3, $+ NaOH$ 7.
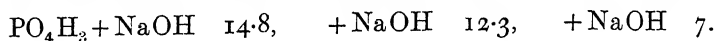
The last number is, however, not quite accurate, as on account of the hydrolysis of trisodium phosphate, PO_4Na_3, for complete saturation the number should be 8·3 instead of 7. But both the small value and the fact of hydrolysis show that the introduction of sodium affects the tendency to take up metal.

The same thing is observed in the case of sulphuretted hydrogen, SH_2, which, though containing two hydrogen atoms, only forms $NaSH$ in aqueous solution even with excess of soda, the compound Na_2S being converted into the same on solution in water.

$$Na_2S + H_2O = NaSH + NaOH.$$
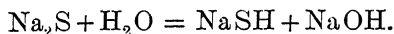
Still more striking is the behaviour of sodium oxide, Na_2O, which is even decomposed by hydrogen :

$$Na_2O + H = NaOH + Na.$$
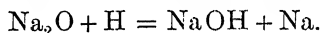
(γ) *Effect of Distance.* It may be added that distance plays a part in the influence of sodium also; in this connexion we may recall the behaviour of fumaric and maleic acids as described in Part II, p. 123, in that the introduction of the first sodium atom into maleic acid, although the stronger acid of the two, exercises a greater influence on the second carboxyl group, because nearer than in fumaric acid; consequently maleic acid is less suited to take up a second atom of sodium than fumaric.

### (c) *Influence of the Heavy Metals, especially Silver.*

Whilst introduction of a light metal hinders its further introduction, that is not the case with the heavy metals such as silver, in accordance with p. 90, but rather the reverse. In this may lie partly the explanation of the fact

that when silver oxide, e. g. is used as a base, all the equivalent hydrogen atoms are replaced, as in sulphuretted hydrogen, fulminic acid, &c., from which, it is well known, SAg_2 and $NCCNO_2Ag_2$ are formed.

2. *Influence of Negative Elements.*

(a) *Influence of Chlorine.*

It is well known that the introduction of chlorine produces or increases acidity, and it will be sufficient amongst inorganic bodies to bring forward the difference between water and hypochlorous acid :

$$HOH \quad \text{and} \quad ClOH,$$
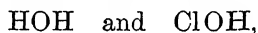
which shows that chlorine replacing hydrogen may convert a neutral compound into an acid. In the organic region this phenomenon recurs often, as is shown, e. g. by the dissociation constants of acetic acid and its chlorine derivatives.

CH_3COOH	$CH_2ClCOOH$	$CHCl_2COOH$	CCl_3COOH
$K = 0.000018$	0.00152	0.0516	1.21
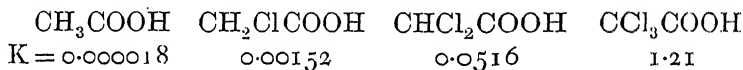
That here also the distance of the chlorine from the hydrogen atom in question is of influence was fully demonstrated in Part II, p. 101, since it was made use of there to decide on constitution. It was shown too how chlorine depresses the basic character of, e. g. aniline. We may here point out a simple series of bodies and their chlorine derivatives :

$$H—H \qquad H—O—H \qquad H_3C—CH_2OH$$
$$Cl—H \qquad Cl—O—H \qquad H_2ClC—CH_2OH.$$
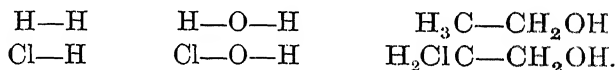
The effect is clearly the most energetic on hydrogen, the strong hydrochloric acid being produced : in water chlorine being further off acts less energetically, the hypochlorous acid produced being less strong; finally, in ethyl alcohol this influence is only to be detected with sharper means of observation, as ethylene chlorhydrin has not a decided acid character.

(*b*) *Influence of Oxygen.*

(*a*) *Oxygen intensifies acidity.* No element possesses this property in so high a degree as oxygen, which indeed owes its name to the favouring influence it exerts on the introduction of metal. In inorganic chemistry the instances are so common that there is no need to quote any, for every oxyacid is evidence of the influence of oxygen in the sense considered. The influence may be followed in detail in the region of organic chemistry.

Facility of carbon for combination with metals. Organic compounds are comparatively rare which are capable of exchanging any of their hydrogen atoms, which are directly united with carbon, for metals. Still such derivatives are well known to be important for synthetic purposes. A case was mentioned on p. 114, in connexion with the effect of hydrogen, viz. that of the acetylides. The majority of others depend on the presence of oxygen.

In carbonic oxide an unmistakable tendency of the carbon to combine with metals is seen, as is proved by the existence of nickel carbonyl, $Ni(CO)_4$, and the corresponding iron derivative.

Secondly, it may be noted that in the group

$$OC-C-CO,$$
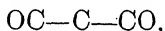
the middle carbon atom has regularly the faculty of combining with metals, e. g. aceto-acetic and malonic esters [1].

$$H_3CCOCH_2CO_2C_2H_5, \qquad H_5C_2OCOCH_2CO_2C_2H_5,$$

in each of these an atom of hydrogen in the CH_2 group may be replaced by sodium, with the aid either of the metal itself or of sodium ethylate.

The same result follows from the combined withdrawal of hydrogen and introduction of oxygen in the group:

$$HC = CH-CO,$$

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[1] *Berl. Ber.* 32. 1876, p. 3398. The constitution of the metal derivative in question is still somewhat uncertain; see *inter alia* A. Claisen's remarks to the German Chemical Society, Dec., 1899.

which also offers an opportunity for introduction of metal in this group CH as in glutaconic ester [1].

$$C_2H_5OCOCH_2CHCHCO_2C_2H_5.$$

If the organic compound contains a hydroxyl group which in any case is accessible to the metals, the addition of oxygen in its immediate neighbourhood, making the carboxyl group

$$O = C - O - H,$$
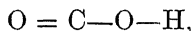
raises this faculty to a pronounced acid character. Further off the oxygen increases acidity if this already exist, as appears from the dissociation constants of acetic, glycollic, glyoxalic, and oxalic acids.

H_3CCOOH	HOH_2CCOOH	$HOCCOOH$	HO_2CCOOH
$K = $ 0·0c0018	0·000152	0·000474	0·1
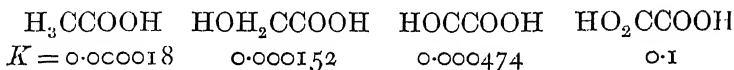
(β) *Oxygen reduces basicity.* Here, again, the number of examples is so great that we will confine ourselves to the nitrogen derivatives, especially organic. The entire change from the strong base, ammonia, to the strong acid, nitric, is shown in the series:

$$NH_3, \quad NH_3OH, \quad NO_2H, \quad NO_3H,$$

as a result of replacement of hydrogen by oxygen.

The same thing may be noted in organic chemistry in the different characters of the amines and amides, which contain the characteristic groups:
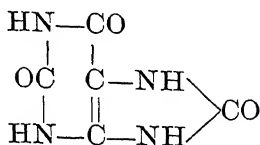
$$C - NH_2 \quad and \quad OC - NH_2,$$
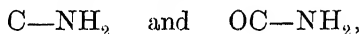
the introduction of oxygen in the latter causes the group almost to lose its basic character.

If the influence goes further, as in the groupings

$$OCNH \quad and \quad OCNHCO,$$
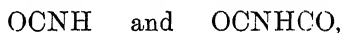
the change is still more marked, and in both cases acids are formed, cyanic in the former, and acids like uric in the latter.

[1] Henrich, *Centralblatt*, 1899, II. 701.

$$\begin{array}{c} HN-CO \\ | \quad | \\ OC \quad C-NH \\ | \quad || \qquad\qquad CO \\ HN-C-NH \end{array}$$

Unfortunately all these observations are merely qualitative, and are often interfered with by other causes, as in the strongly acid character of formic acid, H_2CO_2, as compared with carbonic, H_2CO_3.

(c) Influence of Nitrogen.

(a) *The Cyanogen Group.* The negative character of nitrogen is best seen in derivatives which contain nitrogen as such (not with hydrogen or oxygen), and consequently triply linked to carbon in the cyanogen group:

$$N \equiv C-$$
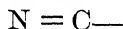
If the element in question has hydrogen attached, forming the amido group (NH_2), its negative character is weakened and is hardly recognizable, or it may even be reversed. If it has oxygen attached as in the nitro group (NO_2), the acid character is indeed sharply marked, but it remains uncertain whether it is to be ascribed to the oxygen or the nitrogen. Therefore we shall first consider the behaviour of the cyanogen group.

In the simplest case, combined with hydrogen to form hydrocyanic acid

$$N \equiv C-H,$$
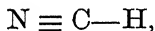
it is apparent that this tendency, caused by nitrogen, of the cyanogen group to attract negative electricity results in the formation of positive hydrogen ions, i. e. of an acid.

Taking then a somewhat less simple case, we may compare cyanic acid with water,

$$NCOH, \qquad HOH,$$

the entry of cyanogen produces here the same effect as that of chlorine, which converts water into a weak acid—hypochlorous acid.

Next let us proceed to the cyanogen substitution products of methane:

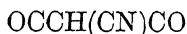$$NCCH_3, \qquad (NC)_2CH_2, \qquad (NC)_3CH,$$
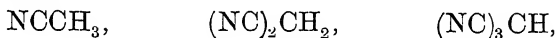
the first, acetonitril, shows no tendency to form salts; the second, malonitril, on treatment with ammoniacal silver nitrates takes up two atoms of silver; the third, cyanoform, is not yet known.

The effect of cyanogen is, however, most striking in this group:
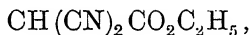
$$OCCH_2CO,$$

which without it is capable of taking up metals (p. 121). The combination

$$OCCH(CN)CO$$

carries such a decided acid character with it that, e.g. cyanmalonic ethyl ester

$$CO_2C_2H_5CHCNCO_2C_2H_5,$$

is capable of decomposing carbonates [1]. Accordingly also dicyanacetic ester

$$CH(CN)_2CO_2C_2H_5,$$

behaves as an acid whose salts can be crystallized out from water [2].

A corresponding joint influence of oxygen and nitrogen is seen, as already mentioned, in the nitro group

$$NO_2.$$

This appears in the somewhat marked acidity of picric acid,

$$C_6H_2(NO_2)_3OH,$$

for example, as compared with phenol. The dissociation constants of the nitrobenzoic acids show the same thing [3]:

Benzoic	o-nitro	m-nitro	p-nitro
0·00006	0·00616	0·000345	0·000396

(β) *Persistence of Negative Character and Valency.* Whilst the multivalent elements appear to form ions with

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[1] *Berl. Ber.* 15. 2244.   [2] Haller, *Compt. Rend.* 111. 53.
[3] Ostwald, *Zeitschr. f. Phys. Chem.* 3. 419.

difficulty, a fact that may be due to the large electric charge associated with these, it is just these multivalent elements, perhaps for that reason, in which the negative character is most persistent. A comparison of chlorine, oxygen, and nitrogen will show this best.

According to p. 84, the negative character of chlorine is the most marked, that of oxygen less, of nitrogen least. But if their respective influences on compounds into which they enter be compared the order will be found reversed, nitrogen giving the group a more decided negative character than oxygen, and chlorine less than the latter.

This may be shown qualitatively by the fact that chlorine does not make carbon capable of combining with metals, chloroform, $CHCl_3$, being perfectly neutral, whilst nitrogen in hydrocyanic acid, NCH, has produced a distinctly acid character ; oxygen does the same, but to a much less extent, in compounds of the type

$$XCOCH_2COX,$$

as in malonic ethyl ester (p. 120). Later some other cases of the kind will be mentioned.

B.   Change in Velocity of Reaction under the Influence of certain Elements and Groups.

Besides the actions brought together above under a single point of view, due to the tendency to ionization which certain elements carry with them into compounds, there are others to be considered, which appear with striking regularity. The former appeared chiefly as displacing equilibrium, since they increase or decrease acidity, and so affect the dissociation constant. The phenomena we have now to consider result in an increase in velocity of reaction, or, as it may be called, in a loosening of the compound. Partly, this action too may be referred to a tendency to ionization, and it will appear in the following, e. g. that introduction of negative groups regularly tends towards breaking up a carbon structure, and that here too the action

of nitrogen is stronger than that of oxygen, and the latter than that of chlorine. But there are also influences that cannot be brought under this heading but point rather to spatial relations.

1. *Acceleration of Reaction that precedes Separation of Ions.*

(a) *Influence of Oxygen.*

In organic compounds oxygen causes in general an increase in velocity of reaction, and tends particularly to overcome the inertia of carbon combination referred to on p. 97. This principle is confirmed in various directions, and only the most important cases need be brought forward here.

Gradually accelerated Oxidation. A striking fact, and one observed in cases outside the carbon compounds as well, is the successively increased facility with which oxygen replaces hydrogen when once partial oxidation has set in.

Amongst organic compounds this gradual facilitation of oxidation is seen most simply in the oxygen derivatives of methane,

$$CH_4, \qquad H_3COH, \qquad H_2CO, \qquad H_2CO_2, \qquad CO_2,$$
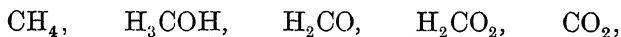
which are successively easier to oxidize, a fact all the more striking since the reverse is true of the chlorine derivatives,

$$CH_4, \qquad CH_3Cl, \qquad CH_2Cl_2, \qquad CHCl_3, \qquad CCl_4.$$
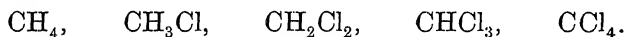
Methane is oxidized with difficulty, as is well known, for not even chromic acid in presence of sulphuric acid does so, although this mixture attacks methyl alcohol; methylene oxide (formaldehyde) oxidizes in air, causing activation of oxygen, and an antiseptic action; it, moreover, reduces silver oxide; finally, formic acid goes a step further in this direction, and will even reduce mercuric oxide. On the other hand, methane is easily chlorinated, methyl chloride less so, and chloroform least.

These specific differences are found again in compounds of the types

$$C_nH_{2n+2}, \qquad C_nH_{2n+1}OH, \qquad C_nH_{2n+1}COH,$$
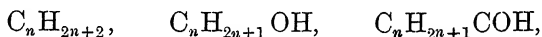
of which the first in association with methane are distinguished by their small tendency to reaction or oxidation, and for that reason called paraffins. The second group in which hydroxyl is present is that of the alcohols, and can be oxidized by a mixture of chromic and sulphuric acids, which is an appropriate means of preparing the higher oxidation products, aldehydes and acids. Further, in the aldehyde group we have a new characteristic in the faculty of reducing silver oxide and formation of a silver mirror with ammoniacal silver oxide solution.

Another fact is connected with this, viz. that in complex compounds oxidation takes place just in the most highly oxidized places, provided the carbon there is associated with hydrogen. If only one carbon atom is oxidized, as in alcohol and aldehydes,

$$H_3CCH_2OH, \qquad H_3CCOH,$$

the new oxygen enters there, forming aldehyde and acetic acid,

$$H_3CCOH, \qquad H_3CCOOH,$$

instead of glycol and oxaldehyde,

$$CH_2OHCH_2OH, \qquad CH_2OHCOH.$$

If there are more oxidized as in aldol,

$$CH_3CHOHCH_2COH,$$

the new oxygen enters at the most oxidized spot, forming oxybutyric acid,

$$CH_3CHOHCH_2COOH$$

and not the ketone aldehyde

$$CH_3COCH_2COH.$$

Something similar is observed in the inorganic region, but cannot be followed out in such detail, on account of

the simpler character of the compounds and the uncertainty of their constitution. We may take as an example the extreme difficulty with which ammonia is oxidized compared with the uncommonly easy oxidation of oxyammonia or hydroxylamine, NH_3O, in consequence of which the latter gains its usefulness as a reducing agent.

Carbon combined with other Elements. We have dealt above with the carbon-hydrogen linkage; the linkage of carbon to other elements, and the reactions possible to it, must now be considered. These are most simply shown in a table:
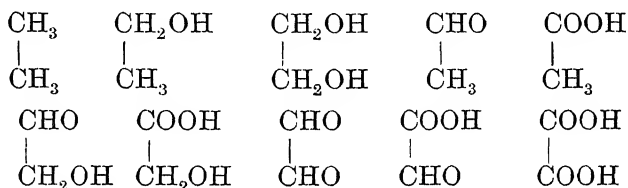
	OCCl	OCOH	OCNH₂	CCl	COH	CNH₂
H Cl		−	−		+	−
H₂O	+		+	−		−
H₃N	+	+		+	−	
HOCH₃	+	+	−	−	−	−
HCOOH	+	−	−	−	+	+

A very large number of possible reactions is indicated by this table, reactions referring to the six groups mentioned at the head of it. Of these six, three have Cl, OH, and NH_2, respectively, united to oxidized carbon, forming the acid chlorides, acids and amides, such as acetyl chloride, acetic acid, and acetamide. The three others contain the same groups attached to non-oxidized carbon, forming the alkyl chlorides, alcohol and amines. It is then striking how the corresponding changes under the influence of HCl, H_2O, H_3N, $HOCH_3$, HCOOH, the two latter typical of the alcohol and acids, occur more easily with oxidized than with non-oxidized carbon, as may be seen from the majority of positive signs, and especially from the great reactivity of the acid chlorides as compared with the alkyl chlorides.

Linkage of Carbon with Carbon. That the linkage of carbon to carbon also is loosened by the presence of oxygen is one of the most general phenomena in organic chemistry, and is especially seen in the fact that all carbon chains on combustion in oxygen break up into unlinked carbon dioxide. There are also in this connexion certain rules

as to the breaking up of carbon chains, of which some may be mentioned here.

In the simplest case, with only two carbon atoms the facility of decomposition increases with the quantity of oxygen contained, as may be seen by comparing the following grades of oxidation:

$$
\begin{array}{ccccc}
CH_3 & CH_2OH & CH_2OH & CHO & COOH \\
| & | & | & | & | \\
CH_3 & CH_3 & CH_2OH & CH_3 & CH_3 \\
\\
CHO & COOH & CHO & COOH & COOH \\
| & | & | & | & | \\
CH_2OH & CH_2OH & CHO & CHO & COOH \\
\end{array}
$$

The last member, oxalic acid, is comparatively easy to decompose, and breaks up on oxidation, and also on heating, either alone or with sulphuric acid, into carbonic and formic acid or carbonic oxide; the seventh member, glycolic acid, also breaks up on heating with sulphuric acid, forming formaldehydes and carbonic oxide. Acetic acid, earlier in the series, needs strong heating with excess of alkali to break it up with formation of methane. The compounds preceding that show the greatest tenacity in the carbon linkage.

In more complex derivatives the consequences of this behaviour are again seen, e. g. in Popoff's rule, according to which ketones,

$$C_nH_mCOC_pH_q$$
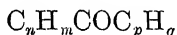
on oxidation break up at the oxidized carbon atom, so that for example dipropylketone,

$$C_3H_7COC_3H_7,$$

goes to propionic and butyric acid, and not to acetic and valerianic. A still more complete break up occurs when two oxidized carbon atoms are attached to another carbon atom, as in aceto-acetic acid,

$$CH_3COCH_2COOH,$$

which forms, with absorption of water, two molecules of

acetic acid ; whilst dibasic acids with both carboxyl groups attached to the same carbon atom, like malonic acid,

$$H_2C\,(COOH)_2,$$

on heating break up with separation of carbonic acid.

If three oxidized carbon atoms are attached to another carbon atom the break up is still easier, and the acid

$$HC\,(COOH)_3$$

is only known as the ethyl ester obtained from sodiomalonic and chlorocarbonic esters, which on saponification leads to malonic acid.

(b) *Influence of Chlorine and Nitrogen.*

The loosening of compounds, or more generally, increase in velocity of reaction, caused by oxygen, and perhaps due to its marked negative character and the ionization associated with that, is observed also in the case of nitrogen and chlorine. As appeared previously, chlorine, though in itself more ·strongly negative than oxygen, is less capable than that element of carrying the negative character into compounds; the same is true here, whilst for nitrogen the phenomena are in both respects reversed.

Dealing only with the effect on the linkage of carbon to carbon, this is weakened by chlorine, as may be seen from Krafft's researches on perchlorination of the saturated hydrocarbons. On repeated heating with iodine chloride all the hydrogen is replaced by chlorine, but at the same time a tendency to break up is observed, so that, e. g. C_3Cl_8, first produced from propane, decomposes afterwards into C_2Cl_6 and CCl_4, whilst, finally, C_2Cl_6 also yields CCl_4. From butane the perchlorinated compound C_4Cl_{10} could not be obtained, and toluene too, after forming $C_6HCl_4CCl_3$, breaks up into C_6Cl_6 and CCl_4. In combination with oxygen the decomposing action of chlorine may be observed in bodies containing the group CCl_3CO, such as chloral,

CCl_3COH, which under the action of alkali yields chloroform.

Combination with nitrogen has a still stronger tendency towards decomposition; this follows the appearance of the cyanogen group, since, e.g. acetonitril, CH_3CN, is decomposed by sodium, cyanogen, $NCCN$, by bases and cyanoformic acid, $NCCOOH$, even spontaneously. The same is true of the nitro group, and leads, e.g. to non-existence of nitroacetic acid, O_2NCH_2COOH, which on saponification of its ethyl ester breaks up into nitromethane and carbon dioxide.

2. Spatial Influences.

(a) Action of Hydrogen during Esterification.

The accelerating influences so far considered come into play at some linkage of carbon, either with another element or with itself. The action of hydrogen we are about to consider is during the formation of esters, taking place according to the equation

$$H_3CCOOH + HOC_2H_5 \quad H_2O + H_3COOC_2H_5,$$

or generally
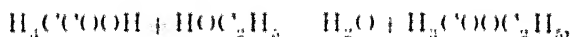
$$XCOOH + HOCY \quad H_2O + XCOOCY;$$

here the carbon combined with oxygen remains so combined, though it may be to another atom, while the principal change happens to the oxygen linkage. Presence of hydrogen and absence of other groups at the point in question produces a most remarkable accelerative action on this reaction, which may be followed in detail, because here in some instances the velocity has been measured under comparable circumstances, and expressed by the velocity constant (Part I, p. 187).

Menschutkin first pointed out the fact, and the following table gives the initial velocities of esterification of different alcohols by acetic acid, i.e. the percentage amount

converted into esters by heating equivalent quantities for an hour at $144°$:

	0	1	2	3	4	5	6	7	8	9
$HOCH_3$	56	–	–	–	–	–	–	–	–	–
$HOCH_2X$ . . .	39	40	47	47	–	–	–	–	–	–
$HOCHXY$ . . .	–	–	–	15	15	22	27	–	–	–
$HOCXYZ$ . . .	–	–	–	–	–	–	0	1	2	1

The table shows the highest initial velocity, 56, for methyl alcohol ; for the primary alcohols from 39 to 47, whilst for tertiary the numbers fall to between 0 and 2. But the numbers are arranged according to the number of hydrogen atoms which are attached to the second carbon, and increase from left to right. Thus, e.g. under the heading 3 for $HOCH_2X$ the number 47 refers to H_3CCH_2OH; under 2 the mean for the alcohols XCH_2CH_2OH, and so on.

Three deductions may be noted : firstly, the accelerative action of the hydrogen attached to the hydroxylic carbon atom, secondly, that even the more distant hydrogen produces a similar effect, and thirdly, that the latter influence is smaller than the former ; thus three more distant atoms raise the value 39 for $HOCH_2X$ to 47, but one directly combined atom raises it to 56.

A similarly arranged table shows that the action on acids, when they are heated with a fixed alcohol, ethyl alcohol, is similar :

	0	1	2	3
$HC\!\!\begin{smallmatrix}O\\OH\end{smallmatrix}$	62	–	–	–
$XC\!\!\begin{smallmatrix}O\\OH\end{smallmatrix}$	6	25	35	46

A second series of investigations by the same author[1] refer to a simpler process of esterification. In the preceding case it is somewhat complicated by the fact that the concentrations are large, and the esterification interfered

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[1] *Zeitschr. f. Phys. Chem.* **I.** 610 ; see also ester formation from acid chlorides, Bruner and Tolloczko, *Acad. de Cracovie*, 1899, 474.

with by the gradual production of water. Both these disadvantages were avoided by Menschutkin in his comparison of the velocities of esterification of the alcohols, because, on the one hand, instead of acetic acid he used acetic anhydride, thus preventing formation of water and the resulting saponification, and, on the other, reduced the concentrations by employing acetone as solvent. Under these circumstances the normal bimolecular process was observed, following the equation (Part I, p. 193),

$$-\frac{dC}{dt} = kC_1C_2,$$

in which C_1C_2 are the concentrations of the alcohol and acetic anhydrides, k the velocity constant, which had at 100° the following values (methyl alcohol, the highest, being taken as 100):

			Quotient	$\dfrac{47\cdot9}{(1\cdot04)^{n-2}}$
I. Methyl alcohol (CH_3OH) . . .		100		
II. Primary normal alcohols (XCH_2OH)				
Ethyl alcohol		47·9		47·9
Propyl alcohol		45·6	1·05	46·1
Butyl alcohol		44·1	1·04	44·3
Heptyl alcohol		37·3	$(1\cdot06)^3$	39·4
Octyl alcohol		35·8	1·04	37·9
$C_{14}H_{30}O$		27·6	$(1\cdot04)^6$	29·9
$C_{16}H_{34}O$		25·5	$(1\cdot04)^2$	27·7
$C_{18}H_{38}O$		23·2	$(1\cdot05)^2$	25·6
$C_{30}H_{62}O$ [1]		16·5	$(1\cdot03)^{12}$	16
II b. Isobutyl alcohol		38·1		
III. Secondary alcohols ($XYCHOH$)				
Dimethyl carbinol		14·1		
Methyl ethyl carbinol . . .		11·6		
Methyl hexyl carbinol . . .		8·7		
IV. Tertiary alcohols ($XYZCOH$)				
Trimethyl carbinol		0·8		

The influence of hydrogen is even more clearly indicated by these numbers than by those already quoted on the initial velocity, and, e.g., the ratio between methyl and ethyl alcohol, formerly 56:47 = 1·2 is here 100:48 = 2.

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[1] The calculated value is here somewhat too small, perhaps on account of the great molecular volume of $C_{30}H_{62}O$, which increases the velocity of reaction.

Whilst, therefore, the distinction between methyl alcohol and the primary, secondary, and tertiary alcohols is more marked, a simple relation appears in the series of primary normal alcohols, since the velocity regularly falls off with increasing distance of the group richest in hydrogen, methyl, and to the extent of 4 per cent. for each inserted methylene group. Here it must be remembered that the velocity of reaction depends, not only on the nature of the reacting body, but on the number of collisions, so that the different rates of diffusion of the alcohols should be considered along with the preceding numbers. It is striking that this varies in a similar manner in other homologous series, as appears from the ionic mobilities of the fatty acids[1]:

	Ionic mobility	Quotient
Acetic acid	43·1	
Propionic acid	39	1·1
Butyric acid.	35·5	1·1
Valerianic acid.	33·5	1·06
Caproic acid	32·1	1·05

If this influence were taken into account, perhaps all the primary alcohols would have the same velocity of esterification.

Velocity of saponification. Let us deal next with the connexion between the velocity constants for esterification (k_1) and saponification (k_2), and the equilibrium constant of the reaction K (Part I, p. 203), i. e. the equation

$$\frac{k_1}{k_2} = K.$$

This follows immediately from the velocity of formation of the ester

$$\frac{d\,C_{ester}}{dt} = k_1\,C_{alcohol}\,C_{acid},$$

and the velocity of saponification

$$-\frac{d\,C_{ester}}{dt} = k_2\,C_{ester}\,C_{water}$$

with the condition that for equilibrium the two velocities must be equal, or

$$k_1 \, C_{alcohol} \, C_{acid} = k_2 \, C_{ester} \, C_{water},$$

whence

$$\frac{k_1}{k_2} = \frac{C_{ester} \, C_{water}}{C_{alcohol} \, C_{acid}} = K.$$

Next, the fact must be taken into account mentioned on p. 116, that the limit of esterification, and therefore K, does not vary much in passing from methyl alcohol to the primary and secondary alcohols, and only sinks notably in the case of tertiary; this is shown by the following numbers, which refer to the alcohols already mentioned (limit on heating with acetic acid to $153°$ to $154°$):

Methyl-,	*Ethyl-*,	*Octyl-*,	*Isobutyl-*,	*Isopropyl-alcohol*
70	67	72	67	61

	Dimethylallylcarbinol		*Phenol*	
	7		9	

It follows from this that, except in the case of the tertiary alcohols, there must be, on the whole, a parallelism between the velocities of esterification and saponification, at least when these are determined under similar circumstances in dilute solution.

The experimental data are insufficient to test these conclusions, and the velocity constants for saponification (k_2), have hitherto only been determined for other, not directly comparable circumstances. Still we shall quote the results in order to make some observations in connexion with them.

The velocity of saponification has been determined in dilute solution in presence of bases or acids. The velocity is only dependent on the specific character of the base in so far as its proportionality to the concentration of the hydroxyl ions indicates; consequently, for strong bases at sufficient dilution, when the electrolytic dissociation may be regarded as complete, it is simply proportional to the concentration of the base, without regard to its nature. So in acids, the concentration of the hydrogen ions is the measure of

activity, and when the acid is strong and sufficiently dilute, is simply proportional to its concentration.

Adopting the equation

$$-\frac{d\,C_{ester}}{dt} = k_2\,C_{ester}\,C_{base},$$

for saponification by bases, the constant k_2 thus appears to be independent of the base, and has been found [1] for ethyl acetate at $9\cdot4°$:

Soda	Potash	Lime	Strontia	Baryta	Lithia
k_2 2·37	2·3	2·28	2·2	2·14	2·21

when normal concentration is taken as unity.

In the same way for acids, with the equation

$$-\frac{d\,C_{ester}}{dt} = k_2\,C_{ester}\,C_{acid},$$

the value of k_2 is independent of the nature of the acid if the latter is strong and sufficiently dilute [2]. At $25°$ we have :

Hydrochloric acid	Hydrobromic acid	Hydriodic acid	Nitric acid
0·0069	0·0062	0·0066	0·0063

Chloric acid	Methylsulphonic acid
0·0065	0·0068

Next, comparing the behaviour of the different esters, we find a fundamental difference according as the saponification is due to base or acid.

For saponification by bases we find a relation among the velocities that distantly recalls that among the velocities of esterification, as may be seen from the following numbers, in which the rate of formation for methyl acetate is taken as 100 :

	Saponification (NaOH) at $9\cdot4°$	Esterification
Methyl acetate	3·49	100
Ethyl acetate	2·31	47·9
Propyl acetate	1·92	45·6
Isobutyl acetate . . .	1·62	38·1

[1] Reicher, *Ann. de Chemie u. Pharm.* 228. 275 ; Ostwald, *Journ. f. prakt. Chem.* 35. 112 ; Arrhenius, *Zeitschr. f. Phys. Chem.* 1. 110 ; Bugarsky, l. c. 8. 418.
[2] Ostwald, *Journ. f. prakt. Chem.* 28. 449.

It is quite different for saponification by acids. The nature of the alcohol has then a very subordinate influence[1]; for the acetic esters with normal hydrochloric acid at 40° the following numbers were observed:

Methyl-	Ethyl-	Propyl-	Isobutyl-	Isoamyl acetate
0·0126	0·0131	0·0129	0·0129	0·0124

Phenyl acetate	Triacetin
0·0076	0·006

On the other hand, the acid has a far-reaching influence, as appears on comparing the velocities for the following ethyl esters:

Ethyl-formate	Acetate	Chloracetate	Dichloracetate
0·253	0·0131	0·0076	0·0122
Trichloracetate	Propionate	Butyrate	Isobutyrate
0·2	0·014	0·008	0·0078

Valerate	Benzoate
0·00276	0·00007

This effect of the acid is far less marked when the saponification is produced by a base; the following numbers are from Reicher for the velocities with soda at 14·4°:

Ethyl acetate	Ethyl propionate	Ethyl butyrate	Ethyl isobutyrate
3·2	2·82	1·7	1·73

Ethyl isovalerate	Ethyl benzoate
0·61	0·83

differences which may very well depend on the different rates of diffusion of the esters.

All these data lead to the conclusion that on saponification by alkali the ester molecule,

$$ZOA$$

is attacked between the alcohol radicle and the oxygen.

[1] Loewenherz, *Zeitschr. f. Phys. Chem.* 15. 395 ; de Hemptinne, l. c. 13. 516. In harmony with this it appears that the effect of temperature on saponification of acetic esters by hydrochloric acid is the same, but not on that of the esters of different acids. Price, *Kongl. Svenska Akad.* 1899, 930.

Assuming that it is essentially the negative hydroxyl ion that acts here, the process would be

$$ZOA + (\overline{HO}) = (ZO) + HOA,$$
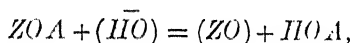
so that the hydroxyl combines with the alcohol radicle (A), and its negative charge is transferred to the acid ion (ZO).

On saponification by acids the attack is between the acid radicle and the oxygen. Assuming that here it is essentially the positive hydrogen ion that acts, the process would be

$$ZOA + (\overset{+}{H}) = (\overset{+}{Z}) + HOA,$$
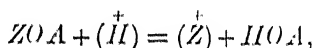
so that the hydrogen ion combines with OA and transfers its charge to the hypothetical residue Z, which then by its action on water reproduces the hydrogen ion,

$$(\overset{+}{Z}) + H_2O = ZOH + (\overset{+}{H}).$$
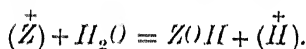
(b) *Other Spatial Influences* [1].

In dealing with the problem of velocities two distinct points of view may be made use of. From the first the necessary relations between equilibrium and velocity, and between the former and temperature, lie in the foreground. The practical execution of the problem is then very complicated and lengthy ; but, on the other hand, the certainty of the basis facilitates any test of a supposed bearing on constitution. Otherwise the velocity may be simply determined for as many reactions as possible, thus substituting a wide extent of data for certainty of theoretical basis. The connexion between the two principles lies in determining the conditions under which the reactions in question run their normal course in time, and whose velocities may, therefore, be exactly expressed by velocity constants.

With the data at present available it is only possible to bring forward some general results and refer these to

[1] Scholtz, *Einfluss der Raumerfüllung der Atomgruppen.* Sammlung von Ahrens, 1899.

a plausible explanation [1]. Thus, with regard to velocity of reaction, the accelerating effect of oxygen, when acting on a carbon linkage, must first be noted, and its possible cause in a commencement of formation of negative ions. A second result of great importance is that in reactions where carbon linkages are not specially concerned, presence of hydrogen has an accelerating effect. That this cannot be due to a tendency to form positive ions is shown by the stability of the saturated hydrocarbons, so that it has been rightly suggested, from several sides, that another cause must be looked for, such as the small volume or small mass of hydrogen. However the facts now to be discussed may be connected with the preceding ones, these considerations of spatial influences start from an entirely different method of research, which must now be described.

Already in Part II, p. 122, we have mentioned, as precursor of stereochemistry, explanations, such as that developed mainly by Wislicenus, of the anhydride formation of maleic acid,

$$HCCOOH$$
$$\|$$
$$HCCOOH$$
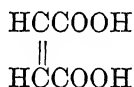
This is easily seen to result from the closeness of the carboxyl groups, in contradistinction to fumaric acid,

$$HCCOOH$$
$$\|$$
$$COOHCH$$
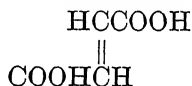
which does not yield an anhydride.

With this is connected the fact that if in maleic acid the hydrogen is replaced by larger groups, so by the greater space occupied the carboxyls are driven closer together, formation of anhydride is so facilitated that, e. g. pyrocinchonic acid,

$$H_3CCCOOH$$
$$\|$$
$$H_3CCCOOH$$

---
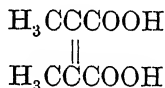
[1] The investigations of Michael (*Journ. f. Prakt. Chem.* (2) 37. 473) only reached me after correcting the proof.

is known only as anhydride,

$$
\begin{array}{c}
H_3CCCO \\
\| \quad {>}O \\
H_3CCCO
\end{array}
$$
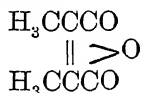
and the anhydride is not attacked by water.

Such hindrance to reaction, due to replacement of hydrogen, which is equivalent to an acceleration of reaction in the presence of hydrogen, was found by Victor Meyer [1] in the region of esterification, in the most striking manner.

First, it appears that if in benzoic acid the two hydrogen atoms nearest the carboxyl group are replaced, esterification almost fails even in excess of methyl alcohol saturated with hydrochloric acid. Representing the position of the carboxyl group by 1, the following numbers were obtained :

$$
\begin{array}{llll}
2.4 & C_6H_3Br_2COOH & \ldots & 95\ \%\ \text{ester,} \\
2.6 & C_6H_3Br_2COOH & \ldots & 0 \quad ,, \\
3.4.5 & C_6H_2Br_3COOH & \ldots & 96 \quad ,, \\
2.4.6 & C_6H_2Br_3COOH & \ldots & 4 \quad ,,
\end{array}
$$

It appeared next that the mass of the radicle placed in the ortho-position is of influence, and that especially heavy ones $(Cl = 35.5, NO_2 = 46, Br_3 = 80, I = 127)$ prevent esterification even at the boiling point, whilst others $(CH_3 = 15, OH = 17, F = 19)$ do so only at atmospheric temperature. This is quite in agreement with Menschutkin's discovery with regard to the initial velocity of esterification of different acids since, e. g. the following are the values for methyl derivatives of acetic acid:

$$
\begin{array}{lr}
H_3CCOOH & 46 \\
H_3CCH_2COOH & 41 \\
(H_3C)_2CHCOOH & 29 \\
(H_3C)_3CCOOH & 8
\end{array}
$$

whilst similar results regarding the alcohols were given on p. 132.

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[1] *Zeitschr. f. Phys. Chem.* 21. 149.

Since in general the limit of esterification varies little with composition amongst the acids, the esters of the diortho-substituted acids also show a very small velocity.

Since the general lines of these striking phenomena have thus been indicated, Goldschmidt [1] followed out further the effect of ortho-substitution by measuring velocities of reaction. When sufficiently diluted with ethyl alcohol the acids suffer under the influence of hydrochloric acid a reaction whose velocity is proportional to the mass of the acid itself, and to that of the hydrochloric acid, thus giving a simple monomolecular equation for the reaction, since the quantity of hydrochloric acid does not change during the experiment.

In this way the influence of the ortho-substituting group appears very clearly, even when only one of the hydrogen atoms in that position is replaced:

Benzoic acid 0·0428	*Phenyl-acetic acid* 3·33		
	ortho	*meta*	*para*
Methylbenzoic acid . . .	0·0111	0·047	0·024
Oxybenzoic acid	0·0021	—	—
Nitrobenzoic acid	0·0028	0·0296	0·0261
Bromobenzoic acid . . .	0·0203	0·0553	0·045

The very great velocity, 3·33, for phenylacetic acid, $C_6H_5CH_2COOH$, in which two hydrogen atoms adhere to the carbon which carries the carboxyl group, falls to 1 per cent. of its value, or 0·0428 for benzoic acid, in which these are wanting. If in the latter the nearest hydrogen atoms, those in the ortho position, are replaced the velocity sinks still further, but without any very remarkable influence due to the mass of the substituting group.

Another series of phenomena that are most probably due to spatial effects, is associated with Pasteur's decomposition of optical antipodes by organisms described in Part II, p. 115. As Emil Fischer found, this decomposition may be produced outside the organism by enzymes, since,

[1] *Berl. Ber.* **20.** 3218.

e. g. the β-methylglucoside from *d*-glucose is easily con-
verted by emulsin into methyl alcohol and grape-sugar
whilst the β-methyl *l*-glucoside is unchanged. The com-
parison of a lock and key was used to illustrate this stereo-
chemical influence [1]. Quite recently a further step in this
direction was taken by Marckwald and McKenzie [2], since
they found that *d*-mandelic acid is esterified more quickly
than *l*-mandelic acid by laevorotatory menthol, whose
constitution is known (whilst the constitution of the
enzymes is still quite in the dark).

§ 3. *Certain Atomic Groupings give rise to entirely new Chemical Properties.*

The relations between chemical properties and constitu-
tion may, in many cases, be referred satisfactorily, though
only in a qualitative manner, to the action of rules : that
elements bring into complex compounds those properties
which they show in their simple derivatives, but are
modified in their action by the other elements already
present in the molecule. That this amounts only to a pre-
liminary insight is shown by the failure of all attempts to
give a quantitative form to the rules in question, expressing
the facts numerically. Thus, e. g. the heat of formation
cannot be determined accurately by addition (p. 103), because
the intensity of combination of two atoms is influenced by
the others present. These influences again can be grouped
and arranged under definite points of view, it is true, but
again cannot be predicted quantitatively ; rather, on this
point only certain approximate rules can be brought for-
ward, which in many cases fail. For instance, the effect
of chlorine on the strength of the chlorinated acetic acid
suggests a quantitative investigation. The affinity of
chlorine for negative electricity is known (p. 90), and must
stand in a quantitative relation to the increase in the

---

[1] See, *inter alia, Zeitschr. f. Physiol. Chem.* 26. 60.
[2] *Berl. Ber.* 32. 2130 ; Fischer and Windans, l. c. 33. 345.

formation of negative ions due to substitution of chlorine, that is, with the increase in dissociation constant of the substituted acetic acids. But it is plain that other factors, hitherto quite unknown, have to be considered, for the introduction of oxygen, which exerts a negative influence fairly generally, i. e. causes or increases acidity, converts, on the contrary, formic acid into the weaker carbonic acid. This residue of facts that cannot be brought under the two main headings is most evident in the cases where a particular atomic group causes chemical properties that cannot even distantly be expected from the atoms themselves and their mutual influence.

First, in this connexion, come the cases in which an element brings new valencies into play. The best known instance is that of the ammonium bases, which are comparable with potash, such as tetramethyl ammonium hydroxide, $(CH_3)_4NOH$, in which nitrogen appears with a fourth and fifth valency. The similarity to potash, due to the strongly positive character of the radicle, $(CH_3)_4N$, may be attributed to the positive influence of the methyl groups, rich in hydrogen : the same may be said to explain the similar behaviour of the phosphorus and arsenic derivatives, and even the sulphonium bases such as trimethyl sulphonium hydroxide, $(CH_3)_3SOH$, are to be regarded from the same point of view.

This attempt at explanation fails, however, for diphenyl iodonium hydroxide, $(C_6H_5)_2IOH$, also a strong base in which also new valencies of iodine play a part : but they are here exerted on phenyl, which otherwise always exerts a negative influence, so that, in the words of the discoverer, Victor Meyer [1], it is astonishing that :

1. Iodine should act as a base-forming element ;

2. A compound which, beside hydroxyl, only contains the otherwise negative radicles iodine and phenyl, should have the properties of an alkaline base ;

3. Phenyl, which does not form with nitrogen and

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[1] *Berl. Ber.* 25. 5c6.

sulphur, ammonium and sulphonium bases, should appear especially suited to form iodonium bases;

4. The new compound shows the greatest similarity to derivatives of certain heavy metals, especially thallium.

But without the appearance of new valencies certain atomic groupings show quite striking and unexpected chemical properties. We need only think of the discovery by Demole of the easy oxidation of unsymmetrical dibromethylene, H_2CCBr_2, and its analogues, which are capable of taking up oxygen at atmospheric temperature, with formation, in the case named, of bromacetyl bromide, $H_2CBrCOBr$. Or, finally, of the vista opened up by Victor Meyer's discovery of thiophene, C_4H_4S, and the fact that the replacement of the group C_2H_2 in benzene by sulphur changes its properties so little that the preparation and properties of thiophene derivatives in part agree almost word for word with those of benzene.

Starting at the beginning of this work with the simple phenomena of chemical equilibrium, which are associated with the fundamental laws of physics, we have arrived, here, at the close of it, at those mysterious relations among which only the wonderful instinct of the chemist can find the way.